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THE MORPHOLOGY OF THE HEAD-CAPSULE OF SOME COLEOPTEROUS LARVAE¹

BY W. E. WHITEHEAD²

Abstract

A comparative study of the external morphology of 46 species of the more common coleopterous larvae. The antennae and ocelli exhibit wide variation. From the fronto-dorsal aspect, the generalized structure of the head is shown, with which may be compared the modifications which occur and which lead to the disappearance of all the sutures separating the different areas found in this region. From the postero-ventral aspect, the heads are divided into two distinct groups, those that possess a gular area and those that do not. Here again, the specialization is compared with the generalized condition. Where a gula occurs, its development is first traced through the series, and then its gradual suppression, due to specialization, is illustrated. The disappearance of sutures causes the head-capsule to become very compact and heavily sclerotized, and this condition is found to be more general and complete in the campodeiform type of larvae.

Introduction

The original purpose of this study was to obtain some data on the phylogeny of the heads of coleopterous larvae. This has not been very successful owing to the difficulty in obtaining long series of any genus or family necessary for such a study. For this reason the subject is discussed from a comparative standpoint. As the order Coleoptera is very extensive and shows a great diversity of form, a long period of time would be necessary to cover more than a small portion of it. There are but 30 families represented in the following pages, but these show what diverse conditions obtain in the head-capsules of the larvae.

Both campodeiform and eruciform larvae occur in the Coleoptera. The former is a term taken from *Campodea*, a genus in the order Thysanura, which represents an early stage in the phylogenetic development of insects and is the more primitive type. Individuals in this group are usually quite active, with horizontal mouth parts and elongate, flattened bodies. The eruciform larvae on the other hand are not as active, the mouth parts are vertical¹ and the body is more or less cylindrical. The form is usually corre-

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lated with the insect's habits. Campodeiform larvae are mostly predacious, which accounts for their activity and great development of the mandibles, whereas the eruciform larvae are usually surrounded by an abundance of food from the time they hatch from the eggs, so that very little activity is necessary. There are also modifications of the eruciform type as in the scarabaeid larvae which develop very heavy bodies and show still less activity. In addition to these there are the apodous larvae found among the boring beetles, in which case there is no need of much movement.

Although the campodeiform larvae are the most primitive from an evolutionary standpoint, they show the greatest specialization as far as the sclerites of the head-capsules are concerned. These structures in the eruciform group are of a very much more generalized nature. Whatever the degree of specialization may be, however, it bears no relation to the condition found in the adult insects, but is an adaptation dependent upon the requirements of the insects during their larval life.

There has been no large amount of work done on the comparative anatomy of coleopterous larvae. With few exceptions, the available literature deals with conditions existing within a family, or even a smaller group. Probably among the most comprehensive are the works of Gage (8), "Larvae of the Coccinellidae," and Hayes (11), "Morphology, Taxonomy and Biology of Larval Scarabaeoidea."

The following discussion, although on a very small scale, will at least give some idea of the wide variation in structure that exists among the larvae in the more common families of the Coleoptera.

List of Species

The following were the available species. They are not arranged in any particular order and the numbers are given only for convenience.

1. *Harpalus honestus*, Carabidae 2. *Carabus nemoralis*, Carabidae 3. *Cicindela* sp., Cicindelidae 4. *Dytiscus* sp., Dytiscidae 5. *Hydrophilus obtusatus*, Hydrophilidae 6. *Pseudophonus pubescens*, Erotylidae 7. *Cantharis* sp., Cantharidae 8. *Gnathocerus punctulatus*, Histeridae 9. *Cercyon* sp., Sphaeridae 10. *Silvanus surinamensis*, Cucujidae 11. *Epilachna borealis*, Coccinellidae 12. *Adalia bipunctata*, Coccinellidae 13. *Passalus cornutus*, Lucanidae 14. *Dorcus parallelepipedes*, Lucanidae 15. *Staphylinus* sp., Staphylinidae 16. *Micro-malthus debilis*, Lymexylonidae 17. *Aulonium* sp., Colydiidae 18. *Synchita* sp., Colydiidae 19. *Silpha tristis*, Silphidae 20. *Scaphidium 4-maculatum*, Scaphidiidae 21. *Thanasimus formicarius*, Cleridae 22. *Dermestes lardarius*, Dermestidae 23. *Tenebrio molitor*, Tenebrionidae 24. *Rhyncophorus cruentatus*, Curculionidae 25. *Anthonomus grandis*, Curculionidae 26. *Balaninus* sp., Curculionidae 27. *Osmoderma scabia*, Scarabaeidae 28. *Allorhina nitida*, Scarabaeidae 29. *Phyllophaga anxia*, Scarabaeidae 30. *Labidomera clavicollis*, Chrysomelidae 31. *Phyllotreta armorica*, Chrysomelidae 32. *Chelymormpha argus*, Chrysomelidae 33. *Leptinotarsa decemlineata*, Chrysomelidae 34. *Cassida vittata*, Chrysomelidae 35. *Malachius bipustulatus*, Melyridae 36. *Anisandrus*

pyri, Scolytidae 37. *Dendroctonus valens*, Scolytidae 38. *Orchesia micans*, Melandryidae 39. *Scobicia declivis*, Bostrichidae 40. *Chrysobothris femorata*, Buprestidae 41. *Acanthocinus obsoletus*, Cerambycidae 42. *Xylotrechus colonus*, Cerambycidae 43. *Prionis laticollis*, Cerambycidae 44. *Saperda candida*, Cerambycidae 45. *Lampyrus* sp., Lampyridae 46. *Agriotes mancus*, Elateridae.

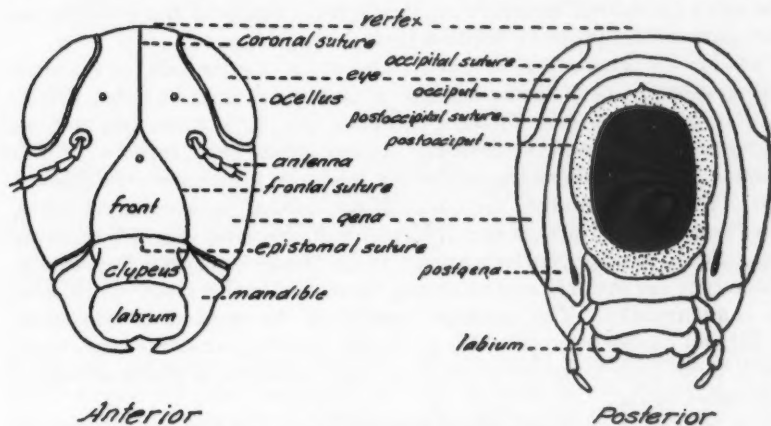
Abbreviations Used in Labelling Figures

acl, anteclypeus	es, epistomal suture	mx, maxilla
an, antenna	fa, frontal apodeme	oa, occipital apodeme
anb, antenna base	fcl, fronto-clypeal-labral area	oc, ocellus
ap, accessory process of antenna	fpr, fronto-parietal	ocp, occiput
as, accessory suture	fr, front	of, occipital foramen
at, anterior pits of tentorium	fs, frontal suture	pcl, postclypeus
bp, basal process of antenna	ge, gena	pg, postgena
cli, clypeal-labral area	gm, gulamentum	po, postocciput
cm, cervical membrane	gs, gular suture	por, postoccipital ridge
cs, coronal suture	gu, gula	pos, postoccipital suture
edm, edge of cervical membrane	lr, labrum	pr, parietal
ep, epicranium	ls, lateral suture	pt, posterior pits of tentorium
epgs, epigular suture	md, mandible	sm, submentum
	mn, mentum	sml, submental lobe
	msm, mento-submental area	smt, submentales
		tu, tubercle

Parts of the Head-capsule

Under this heading are included those parts other than the fronto-clypeal and the postero-ventral regions which are dealt with separately.

The accompanying diagrams illustrate the generalized structure of an



General structure of head (modified from Snodgrass).

insect's head. The chitinous walls of the head-capsule constitute the epicranium and this is divided by sutures into various sclerites. The vertex is marked by a median coronal suture that turns downward and divides into the frontal sutures which extend to the anterior articulations of the mandibles. The coronal suture and the frontal sutures constitute the epicranial suture. The median facial region between the frontal sutures is the frons, ventrad to which, and separated from it by the epistomal suture, is the clypeus, with the labrum suspended from the lower margin of the latter.

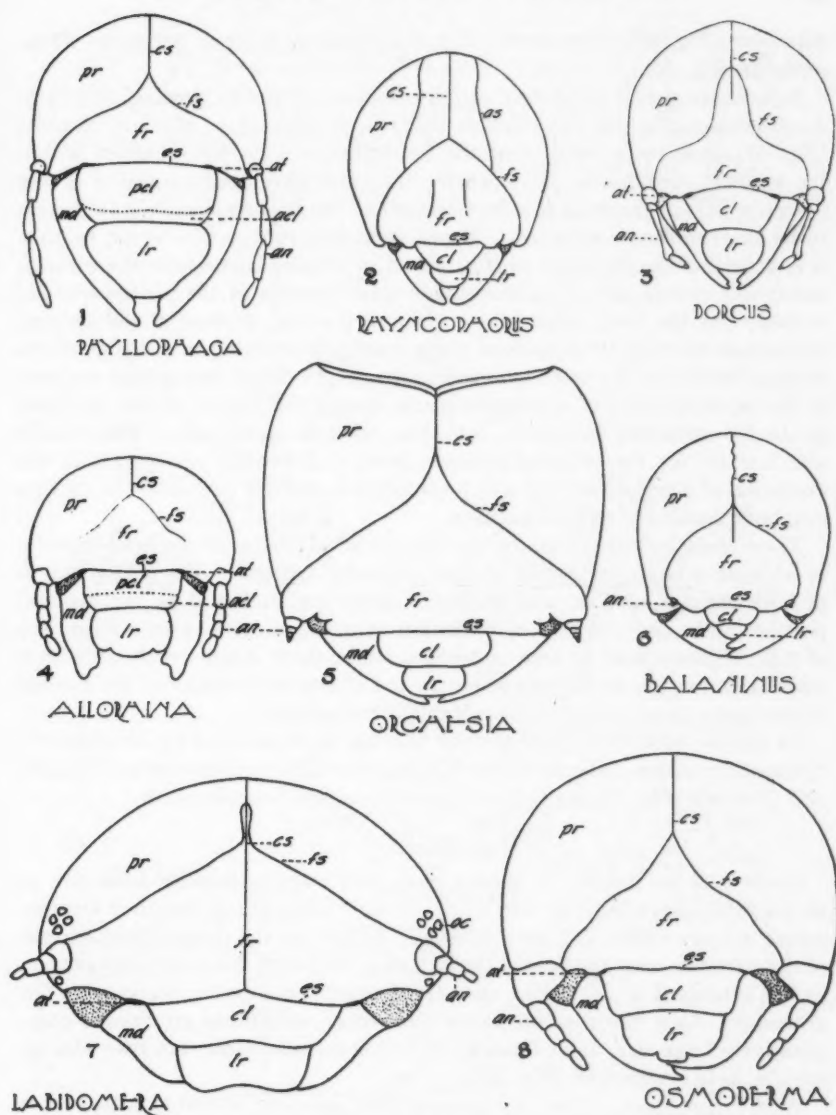
A large portion of the posterior surface of the epicranium is occupied by the occipital foramen. Surrounding this opening dorsally and laterally is the occipital area, the anterior limit of which is defined by the occipital suture. Another suture, the postoccipital, separates the narrow, marginal postocciput to which the cervical membrane is attached. The dorsal part of the occipital area anterior to the postocciput is termed the occiput, and the latero-ventral parts, the postgenae. To the ventral margin of the occipital foramen is attached the labium.

The lateral areas of the epicranium between the occipital suture and the frontal sutures, and separated dorsally by the coronal suture, are termed the parietals. The parietal area behind and below the compound eye is the gena, that between the eyes is the vertex.

In all the more generalized species of larvae studied there is nothing peculiar about the head, it is held more or less vertically with the occipital foramen located posteriorly. As specialization develops, however, we find this condition changed in many groups, the head becomes uptilted so that it is held in a horizontal position with distinct dorso-ventral compression in many species and invariably a change in the position of the occipital foramen. There is no connection between this specialization and that found in adult Coleoptera, in fact a complete reverse condition often exists, as in the case of the adephagous beetles, which are considered to be among the most generalized and have some of the most specialized structures in the larvae. Many of the polyphagous beetles show quite primitive structures in the larval stages.

It will not be necessary to mention many of the species used, as a similar condition exists in all of them, suffice it to say that it is to be noted that in such species as *Dorcus* (Fig. 3) and *Osmoderma* (Fig. 8) to name only two, we find a generalized condition present. Among other head capsules of this type there are a few characteristics which might be mentioned. In *Rhynchophorus* (Fig. 2) for instance, the parietals are crossed by accessory sutures, and in *Pseudophonus* (Figs. 27 and 27A) and in *Hydrophilus* (Fig. 30) there are lateral sutures, neither of which appear to be of any structural importance, although they are the only species among those used in this study which show these characteristics. The posterior margin of the dorsum in *Phyllotreta* (Fig. 20) and *Chelymorpha* (Fig. 23) are deeply notched, while the latter bears on each dorso-lateral margin a group of four tubercles, a characteristic of certain other larvae.

The retraction of the head-capsule within the cervical membrane is a point



FIGS. 1-8.

of interest and shows different degrees of development in the series. According to Snodgrass (17), the postoccipital ridge in some larvae develops into an apodemal plate, shown in *Phyllophaga* (Fig. 45) and which is mostly covered by the cervical membrane. This condition is also shown in *Dorcus* (Fig. 47),

Allorhina (Fig. 48), *Osmoderma* (Fig. 52), and, to a lesser degree, in *Rhynchophorus* (Fig. 46).

In another group consisting of *Chrysobothris* (Fig. 12), *Scobicia* (Fig. 13), *Acanthocinus* (Fig. 16), *Xylotrechus* (Fig. 9), *Prionis* (Fig. 15) and *Saperda* (Fig. 11), it is to be noted that the head-capsule is deeply retracted within the cervical membrane. To consider that this enveloped condition of the posterior part of the head is a development of the apodemal plate would seem to be an erroneous conclusion. A more probable explanation would be that it is a further development of that found in *Phyllophaga* where the cervical membrane covers only a comparatively small portion of the postero-ventral surface. As the head assumed a horizontal position, instead of the cervical membrane covering the apodemal plate, gradually receding to the edge of the occipital foramen, it remained stationary, and the dorsal and lateral surfaces of the posterior part of the head-capsule during the course of the uptilting gradually retracted backward into the cervical membrane. This would also account for the occipital foramen being in a ventral position, with the exception of *Chrysobothris*, in which species it is directly posterior but cutting into both dorsal and ventral surfaces.

There seems to be little doubt that the retracted portion of the head-capsule, or at least a large portion of it, was originally exposed. The sclerotization of both areas is similar, and sutures in some species found on the exposed portion can be distinctly traced backward on to the retracted area. Examples of this condition may be seen in *Scobicia* where there is apparently a distinct coronal suture, also in *Saperda* where we find a faint continuation of the coronal suture and a distinct prolongation of the lateral sutures.

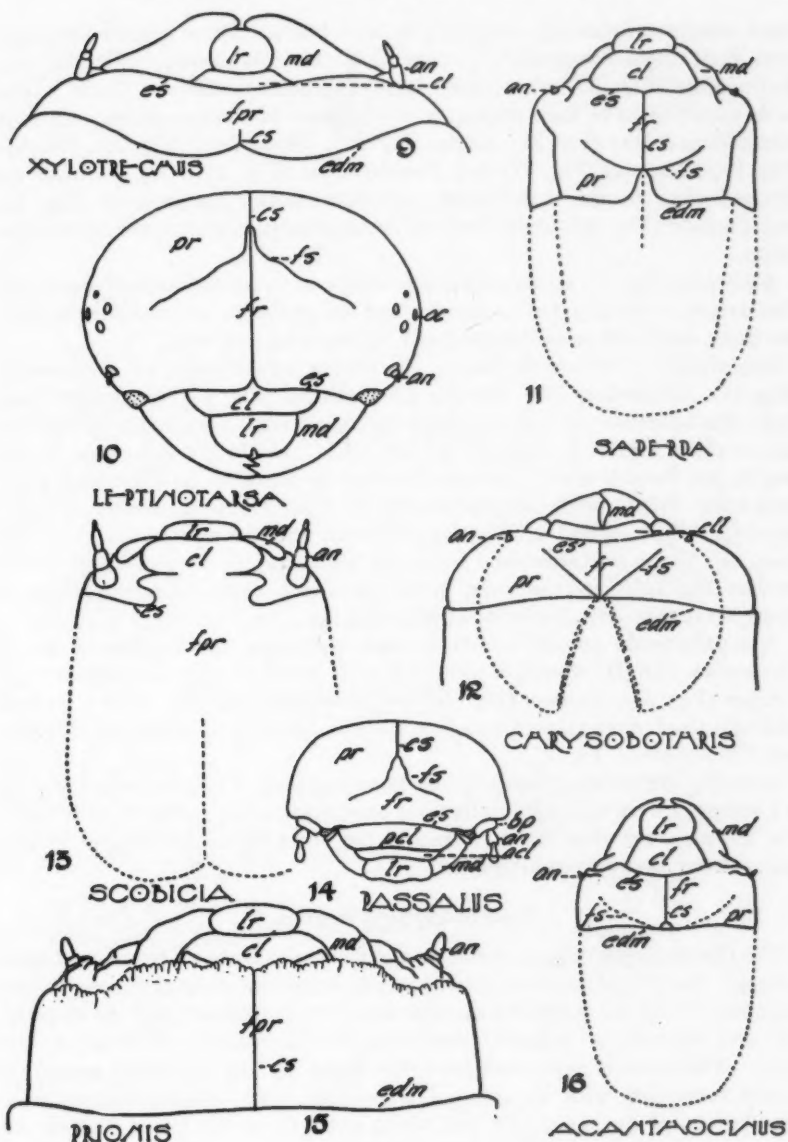
Of species, other than those already referred to, whose head has attained the horizontal position, little more can be said, other than in *Hydrophilus* (Fig. 30) and *Cicindela* (Fig. 36) examples of a dorsal occipital foramen occur.

Ocelli

Ocelli may be present or absent, they may vary in number from one to six pairs (*Hydrophilus*, Fig. 30); there is a wide range in size and their location varies to some extent. They are usually located on the dorso-lateral margin of the parietals near the base of the antennae, although this is not always true, as in *Cicindela* (Fig. 36), where they are situated considerably posterior to the antennae. As a rule they are easily discernible, sometimes attaining a comparatively large size, as in *Dytiscus* (Fig. 33) and *Cicindela*, but may also be minute, as in *Scaphidium* (Fig. 31).

Where more than one pair are present, their grouping is used to some extent in the classification of the larvae. They may be close together and evenly spaced as in *Staphylinus* (Fig. 41) and *Harpalus* (Fig. 32), or separated into groups, a characteristic in *Scaphidium* and *Labidomera* (Fig. 7), or again, they may be close together and arranged on a prominence as shown in *Carabus* (Fig. 34).

It is among the boring larvae and those that have a subterranean habitat, that we find the forms having no ocelli.



FIGS. 9 - 16.

Antennae

As in other characters, the antennae exhibit much variation. They are located in the cephalo-lateral area of the head-capsule, the frontal sutures,

when complete, invariably extending to their bases. There is some departure from their usual location in *Cercyon* (Fig. 44), *Staphylinus* (Fig. 41) and *Hydrophilus* (Fig. 30) where they have migrated medially. There is also some variation as to their proximity to the bases of the mandibles. In such examples as *Silpha* (Fig. 28), *Adalia* (Fig. 39), *Thanasimus* (Fig. 26), *Tenebrio* (Fig. 19), *Harpalus* (Fig. 32) and *Pseudophonus* (Fig. 27), the antennae are situated close to the mandibular articulations, but *Leptinotarsa* (Fig. 10) and *Cassida* (Fig. 43) show them to be situated posterior to the mandibular joints.

Malachi (Fig. 17) shows a unique condition as far as this series is concerned. The antennae are situated in cavities and are probably protrusible, although this point could not be ascertained with the material available.

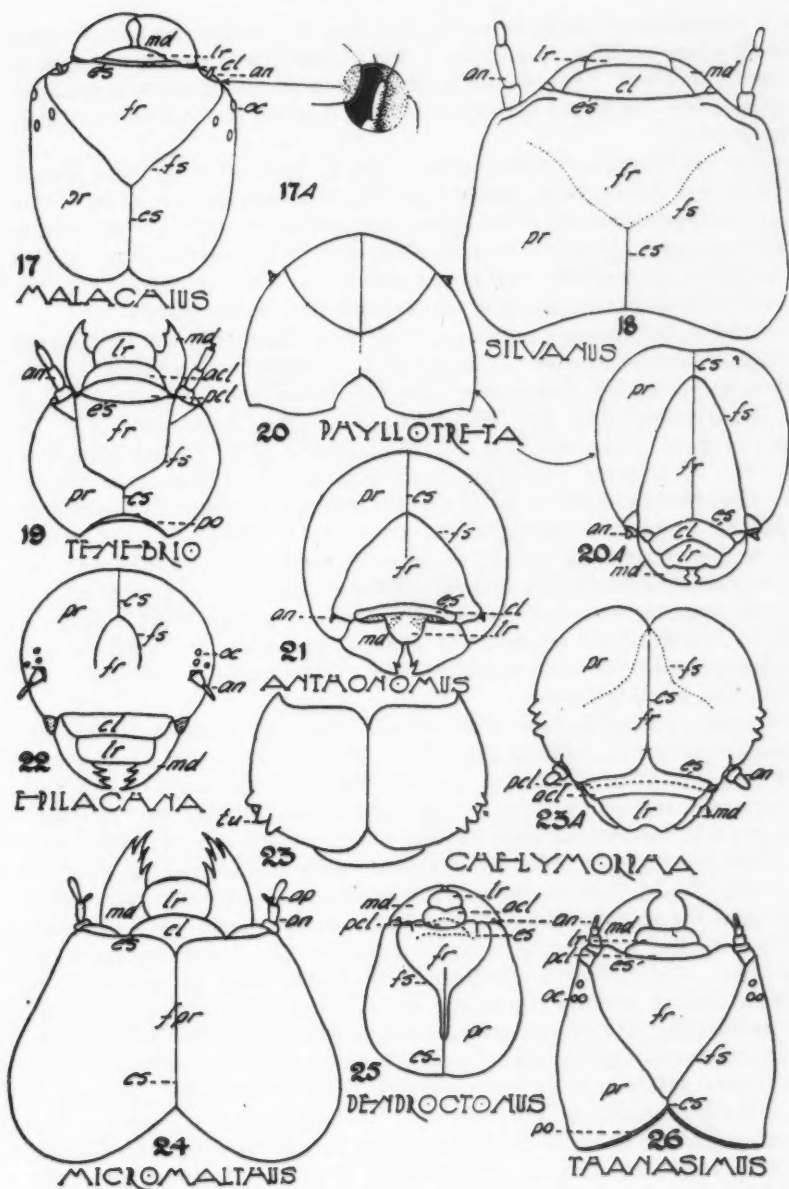
Size shows a very wide range. In boring larvae such as *Anthonomus* (Fig. 21), *Anisandrus* (Fig. 35) and *Chrysobothris* (Fig. 12), to mention only three, the antennae are minute, and from these there is a gradual increase in size to those found in *Silpha* (Fig. 28). Not only is the difference in the length, but there is also a marked difference in diameter, as illustrated when comparing *Silpha* with *Scaphidium* (Fig. 31). There is usually a basal process, well illustrated in *Passalus* (Fig. 14), and the segments attached to that, and which are numbered from the base, may be conical as in *Chelymormorpha* (Fig. 23A), and the boring larvae, globular in *Passalus*, or elongate as in *Staphylinus* (Fig. 41), *Silpha*, or *Dorcus* (Fig. 3).

A supplemental process occurs on some antennae, the location of which also varies. In *Micromalthus* (Fig. 24) it is found on the first segment, in *Cercyon* (Fig. 44), *Agriotes* (Fig. 29) and *Aulonium* (Fig. 40) on the second, while the third antennal segments bear them in *Staphylinus*, *Harpalus* (Fig. 32) and *Pseudophonus* (Fig. 27).

The only species which has apparently no antennae is *Rhyncophorus* (Fig. 2) and although a careful examination has been made it has failed to reveal any. The antennae are very inconspicuous in the other boring larvae, but in this species have disappeared altogether.

Fronto-clypeal Region

The fronto-clypeal region includes, typically, the front or frons, that area between the frontal sutures which extends from the coronal suture to the neighborhood of the anterior articulations of the mandibles, and the clypeus, that area ventrad, or cephalad, depending on the angle of the head, to the front. This area is separated from the front by the epistomal suture, a groove coinciding with an internal transverse ridge between the anterior articulations of the mandibles and which strengthens the lower edge of the face. It has been suggested by some writers that the clypeus was an articular region between the front and the labrum and which secondarily developed into a sclerotized plate. Snodgrass (17) however, disproves this by the fact that the most anterior muscles of the stomodeum have their origin upon the inner surface. The clypeus often shows some differentiation in being divided by a



FIGS. 17 - 26.

partial or complete suture into an anteclypeus, a more or less membranous area next to the labrum, and a postclypeus adjacent to the front.

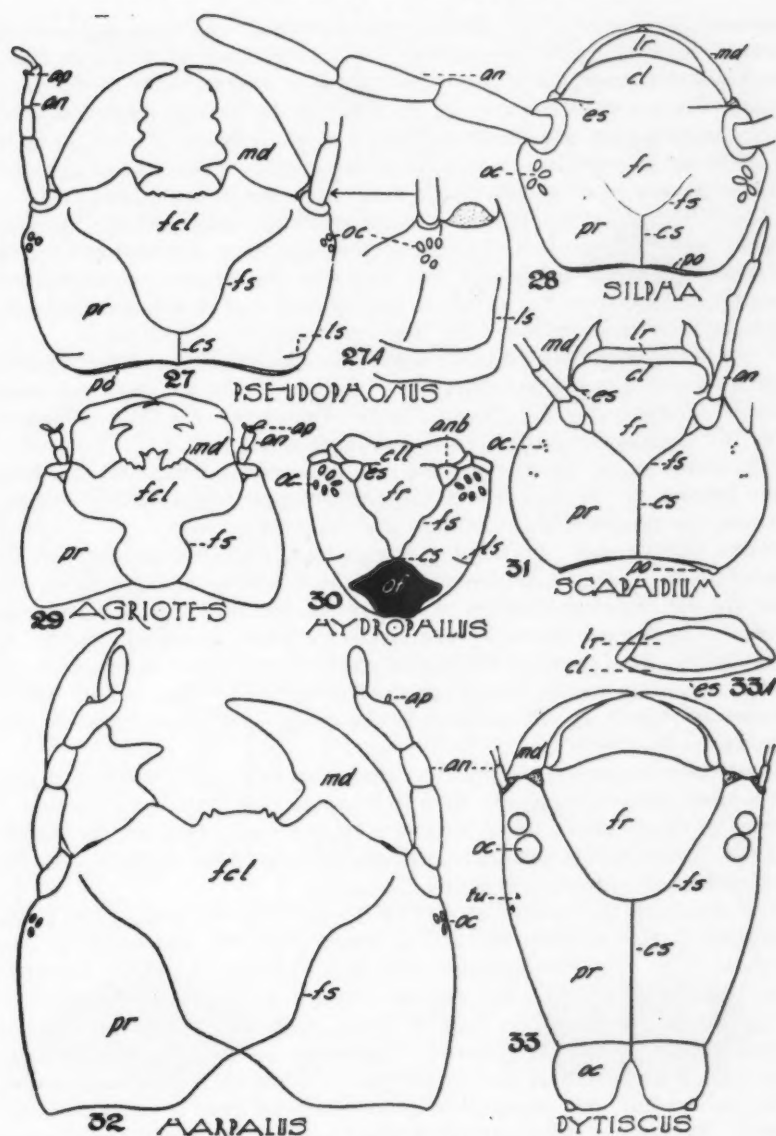
For convenience it might be well at this time to mention the labrum, since in cases where modifications occur in the fronto-clypeal region this area is frequently involved. The labrum, unlike the two preceding parts, is movable, hangs as a free flap before the mouth, and is attached to the anterior margin of the clypeus.

Of the head-capsules under consideration, a typical fronto-clypeal area is singularly well illustrated in *Phyllophaga* (Fig. 1) a species which, as far as this region is concerned, shows a very generalized condition, and on which all the previously mentioned points may be observed. While several other species are as typical, it might be well to use this one as a standard by which the various modifications occurring in other species may be compared.

In order to facilitate analysis, species showing similarities will be grouped together as much as possible. The first group includes *Dendroctonus* (Fig. 25), *Anthonomus* (Fig. 21), *Thanasimus* (Fig. 26), *Osmoderma* (Fig. 8), *Orchesia* (Fig. 5), *Tenebrio* (Fig. 19), *Phyllotreta* (Fig. 20A), *Labidomera* (Fig. 7), *Dorcus* (Fig. 3), *Balaninus* (Fig. 6), *Rhyncophorus* (Fig. 2) and *Malachius* (Fig. 17). All of these species have a full complement of parts in the region under discussion and it will be found that the frontal sutures are fully developed. *Osmoderma*, *Tenebrio* and *Dermestes* are very similar to *Phyllophaga*, but certain slight modifications occur in some of the other species. These are concerned with the coronal suture which extends beyond the union of the frontal sutures on to the front for varying distances. In *Dorcus* it is quite short, somewhat longer in *Balaninus*, *Anthonomus* and *Dendroctonus*, while in *Phyllotreta* and *Labidomera* it extends to the epistomal suture. The clypeus is very suppressed in *Malachius*, but is still intact.

The second grouping consists of *Silvanus* (Fig. 18), *Epilachna* (Fig. 22), *Leptinotarsa* (Fig. 10), *Passalus* (Fig. 14), *Allorhina* (Fig. 4), and *Chelymorpha* (Fig. 23A). In these species too are to be found all the parts of a typical fronto-clypeal region, but the frontal sutures are incomplete. *Passalus*, *Epilachna* and *Leptinotarsa* show distinct but shortened sutures; in *Silvanus* and *Allorhina*, they are becoming indistinct, while in *Chelymorpha* they are only vestigial. In *Chelymorpha* also, it is to be noted that the frontal sutures originate at the posterior margin of the head and the coronal suture extends to the epistomal suture, the latter modification also being applicable to *Leptinotarsa*. In *Epilachna*, Underhill (19) figures what is apparently a double coronal suture and the frontal sutures closely converging near their distal extremities, all of which are indicated as being quite definite. He also shows a double epistomal suture. Gage (8) does not find this condition existing in the coronal suture or in the epistomal region, neither were they observed in the specimens examined by the writer.

Another group consists of *Scaphidium* (Fig. 31), *Silpha* (Fig. 28), *Cassida* (Fig. 43), *Anisandrus* (Fig. 35), *Micromalthus* (Fig. 24), *Aulonium* (Fig. 40) and *Adalia* (Fig. 39), because each shows a tendency towards reduction in sutures, or because there is an apparent complete disappearance of some part as compared with the primitive type. Of these, *Scaphidium* is the only one



FIGS. 27 - 33A.

having complete frontal sutures, those in *Adalia* are almost so and those in *Aulonium*, which is minus a coronal suture, show somewhat less development, while they are only vestigial in *Silpha*. In *Anisandrus* the sutures have dis-

appeared, leaving only the coronal suture, in which case frons and parietals combine to form the fronto-parietals. A similar condition exists in *Micromalthus* and *Cassida*, but in these, the coronal suture extends to the epistomal suture. Such a condition may be the result of the forward migration of the frontal sutures, but this would not hold with the views of Barber (1) as far as the larval *Micromalthus* is concerned, as he believes this species to have a distinct clypeus, in which case the dividing suture would be the epistomal.

Apart from these modifications of the epicranial suture, all the foregoing species, with the exception of *Cassida*, show that there is a tendency for the epistomal suture to disappear. The suture in *Anisandrus* can be followed throughout its course, but in the remaining four species it has entirely disappeared with the exception of the lateral portions.

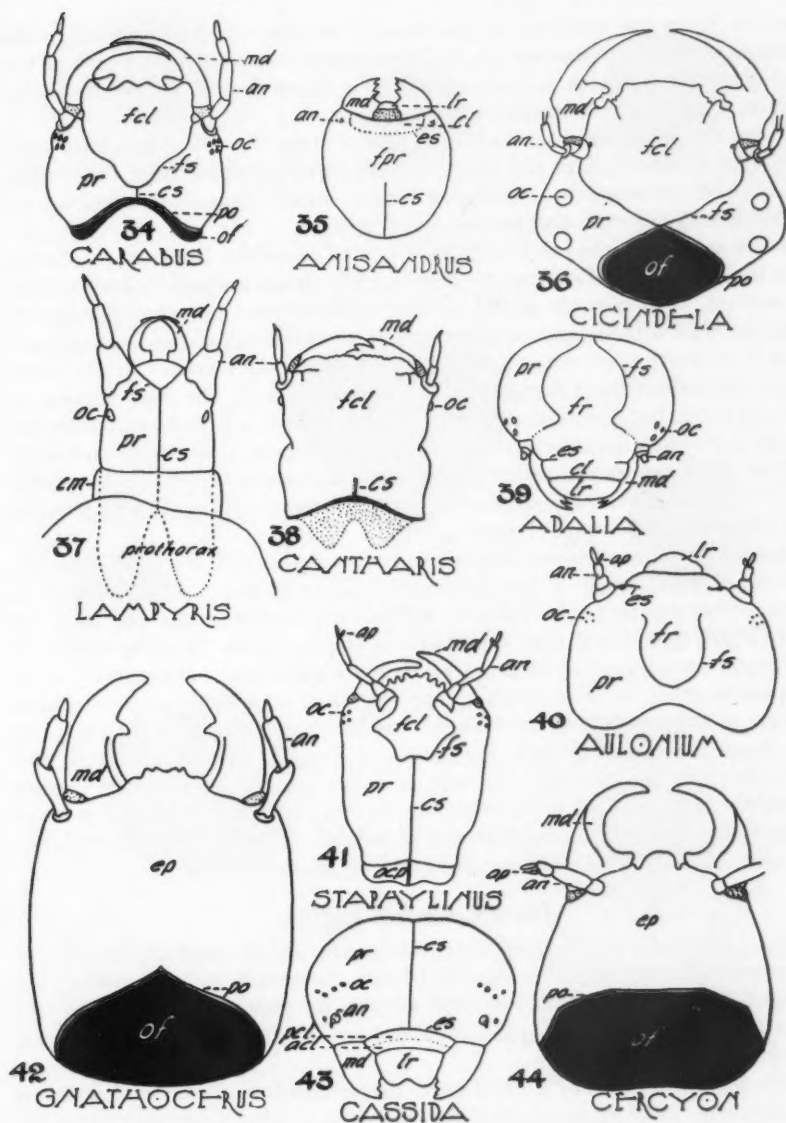
Some of the wood-boring larvae show certain modifications and the following representatives are grouped together on account of the nature of the head-capsule. (*Saperda* (Fig. 11), *Prionis* (Fig. 15), *Xylotrechus* (Fig. 9), *Acanthocinus* (Fig. 16), *Chrysobothris* (Fig. 12) and *Scobicia* (Fig. 13).)

The retraction of the head-capsule into the cervical membrane may have some bearing on the structure of the fronto-clypeal region, as the distance between the margin of the membrane and the anterior extremity of the head becomes considerably shortened. *Saperda* and *Chrysobothris* are perhaps nearest to the typical condition as far as the frontal sutures are concerned, they are not complete in either of the species, but they are least definitely shown. The coronal suture in each instance extends throughout the length of the front. In *Anthocinus* the frontal sutures have almost disappeared and in the remaining species they have done so entirely. The coronal suture persists in *Prionis*, is very reduced in *Xylotrechus* and has completely disappeared in *Scobicia*.

The epistomal sutures are intact in all species except in *Scobicia* and here the median portion is missing. It is to be noted that there is a reduction of sutures in *Chrysobothris*, but it is apparently the suture between the labrum and the clypeus that is absent as, from the position of the tentorial pits, the epistomal suture appears to be intact.

The remaining species studied may be divided into two groups, the larger consisting of *Hydrophilus* (Fig. 30), *Cicindela* (Fig. 36), *Carabus* (Fig. 34), *Harpalus* (Fig. 32), *Pseudophonus* (Fig. 27), *Dytiscus* (Fig. 33), *Lampyrus* (Fig. 37), *Staphylinus* (Fig. 41), *Agriotes* (Fig. 29) and *Cantharis* (Fig. 38).

Hydrophilus perhaps shows the least specialization in the fact that there is at least a slight differentiation between the labrum and the clypeus. *Dytiscus* may also be mentioned in this connection as, while no labrum can be seen from the dorsum, this structure may be observed from a cephalo-ventral aspect. *Staphylinus* and *Lampyrus* show a fusion of the labrum and clypeus, but in the others, with the exception of *Cantharis* and *Cicadela*, each of which has what are evidently vestiges of sutures, there is no differentiation between the front, the clypeus and the labrum. It is to be noted in all species in this group that the frontal sutures are very well defined and in most instances



FIGS. 34 - 44.

complete. A major character in *Agriotes* is that the cephalic margin is tridentate.

The last two species, *Gnathocerus* (Fig. 42) and *Cercyon* (Fig. 44) are the most specialized of all, the epicranium being entirely devoid of sutures.

Cercyon bears two notches on the anterior margin which are probably the remains of some previous suture, and *Gnathocerus* has an extended area at the cephalic margin, which is also notched to a lesser degree, but there are no sutures apparent to differentiate the parts.

From the foregoing discussion it will be obvious that there is a very wide variation of structure in the fronto-clypeal region, ranging from the simple, generalized condition in *Phyllophaga*, to a highly specialized structure as found in such species as *Cercyon* and *Gnathocerus*.

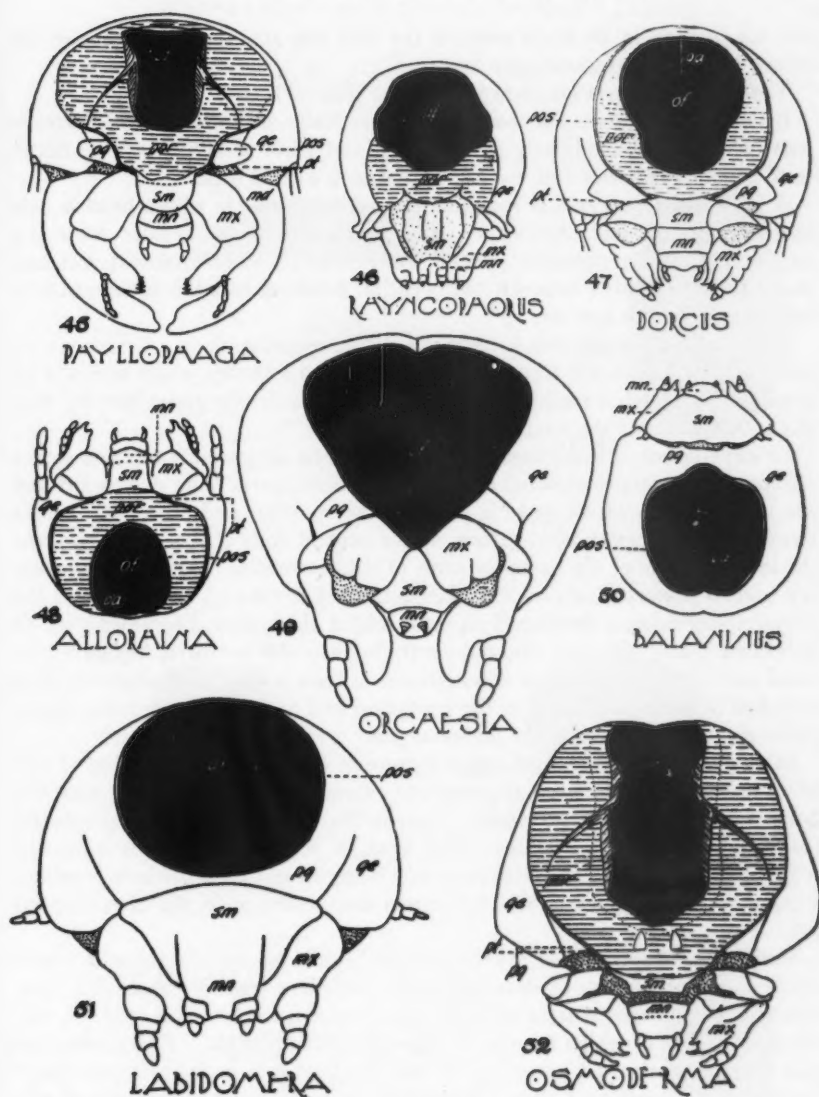
In his work with the head-capsules of adult Coleoptera, Stickney (18) found that in the majority of species, the development trends towards the obliteration of sutures, consequently giving greater compactness and consolidation of sclerites, with a tendency towards stronger sclerotization of the head-capsule. This is all quite applicable to the head-capsules of the larvae. In the eruciform and melolonthoid forms, we have species showing the least amount of sclerotization, but the most complete conditions from a primitive standpoint. At the same time the obliteration of sutures has begun in the disappearance of part or all of the frontal sutures, resulting in a fronto-parietal region, as well as at least the partial disappearance of the epistomal suture, leading towards the formation of a fronto-clypeus.

Among the campodeiform larvae is to be found a gradual increase in specialization, culminating in a complete consolidation of parts. Such species as *Hydrophilus* are probably the most generalized in this group, but they are more highly specialized than the eruciform species, while the other species in the group show a gradual tendency towards the obliteration of sutures. With this obliteration, comes a much greater degree of sclerotization, the cephalic margin of the most highly specialized forms being very marked in this respect. No doubt the habits of the larvae have something to do with the amount of sclerotization they possess, although it seems natural that as the sutures disappear there should be a tendency towards the strengthening of these areas. The degree of disappearance of sutures seems to coincide with the degree of sclerotization, as illustrated in the clypeo-labral area.

Postero-ventral Region

If all the parts of the postero-ventral region of the head-capsule are to be mentioned, they would include the labrum, the maxillae, the postgenae, the occiput, the postocciput, and in some species, the gula. The mandibles also have a ventral or posterior articulation and are frequently observed from this aspect.

The labium consists of a basal part, the submentum, anterior to which is the mentum, to which is attached the eulabium, or what Crampton terms the prementum, which bears the palpi. In the more generalized insects, the labium hinges to the posterior part of the head, completing the ventral margin of the occipital foramen, and on either side of it are to be found the proximal parts of the maxillae, and, depending on the nature of the occipital foramen, the anterior median portions of the postgenae.



FIGS. 45 - 52.

The maxillae are complicated gnathal appendages situated in the membrane on either side of the labium.

The postocciput which is a narrow sclerite surrounding the occipital foramen and the postoccipital suture, which separates it from the occiput, is an important landmark of the head. It is usually present and the posterior tentorial

pits are located in its lower ends; if the pits migrate, the lower ends of the suture become correspondingly longer.

The foregoing parts are shown in *Dorcus* (Fig. 47).

In generalized insects the heads are held vertically, in which case the posterior part of the head is naturally rather short, and while modifications do occur, they are not as profound as in insects possessing a gular region.

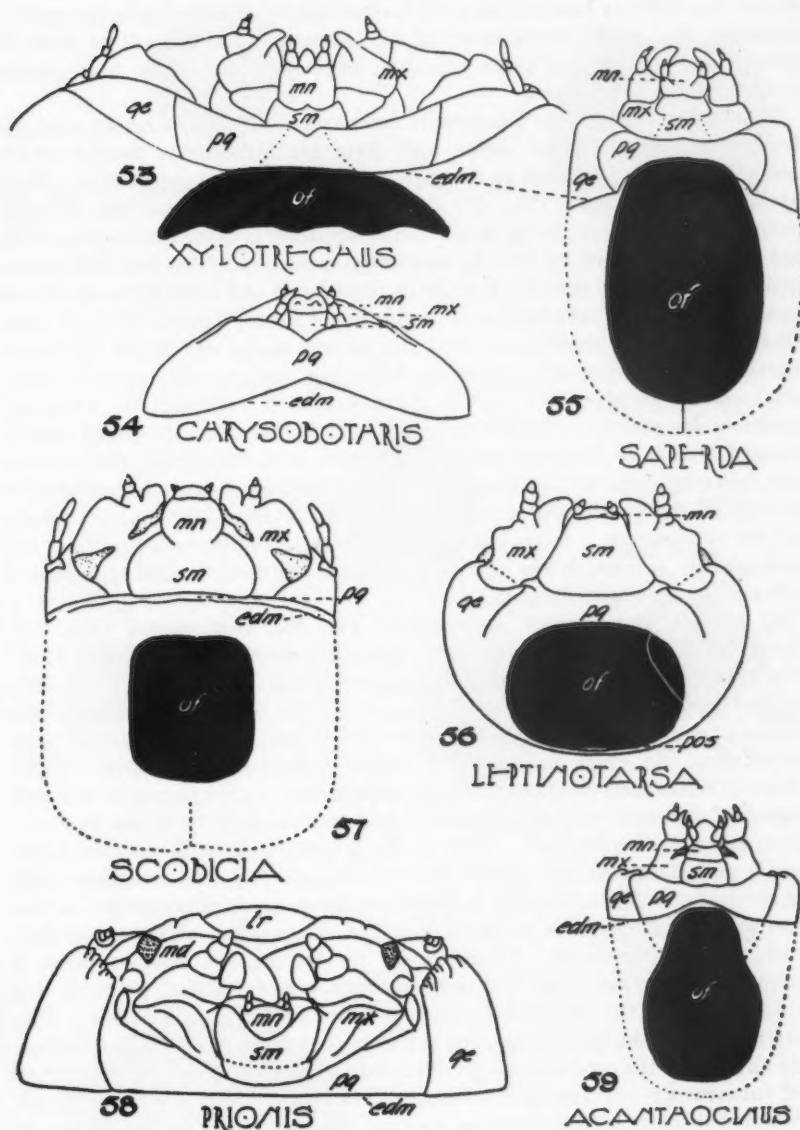
A fully developed gula is found chiefly in those insects whose head is held horizontally, and not always then, and as this condition develops there is a lengthening of the posterior part of the head, the labium moving forward, thus causing the area between the occipital foramen and the submentum to become very much greater.

The origin of the gula has long been a controversial subject. Crampton (7) and later Snodgrass (17) have, however, advanced a theory which seems to be generally accepted, a modified account of which is briefly given here by way of partly explaining the modifications that occur.

In some larvae, *Phyllophaga* (Fig. 45) would be an example of those under discussion, the face is directed forward, the mouth parts hang downward and the under surface of the head is short. The occipital and postgenal regions terminate in a postoccipital suture, in the ventral ends of which are situated the invaginations of the posterior arms of the tentorium. Beyond the suture is a narrow postoccipital rim of the cranium, best developed ventrally, and the postoccipital ridge is developed on each side of the occipital foramen into an apodemal plate, the two uniting ventrally into the tentorial bridge. The basal part of the submentum is sclerotized to form a triangular plate which is attached to the mesal points of the postgenae and has its extreme basal angles prolonged to points behind the tentorial pits.

In *Silpha* (Fig. 70), the general structure of the head is similar, but it will be observed that the ventral postgenal margins are much longer and the posterior tentorial pits are drawn towards the medial line in the prolonged basal angles of the postgenae. The base of the submentum is narrowly constricted behind the tentorial pits, which almost cut off a distinct proximal area, the lateral angles of which become continuous with the postoccipital rim.

The extreme basal area of the submentum is the beginning of the gula which reaches various degrees of development in different species. It is that area between the posterior margin of the submentum and the occipital foramen, the distal extremity of which may be designated as the pregula. Externally, the gula may be marked off anteriorly by the tentorial pits (gular pits), although Crampton has advocated that a line drawn from the basal articulation of one cardo to the other might be preferable to using such shifting landmarks as the gular pits. With the uptilting of the head and the necessary prolongation of the ventral area, the gular pits tend to move forward, under which conditions the gula would become proportionately longer. The gula is bounded laterally by the gular sutures, on or near which are situated the gular pits. On either side of the gula are the postgenae, or what are termed the paragulae by



FIGS. 53 - 59.

Crampton, who also differentiates the anterior portion as being the hypostoma.

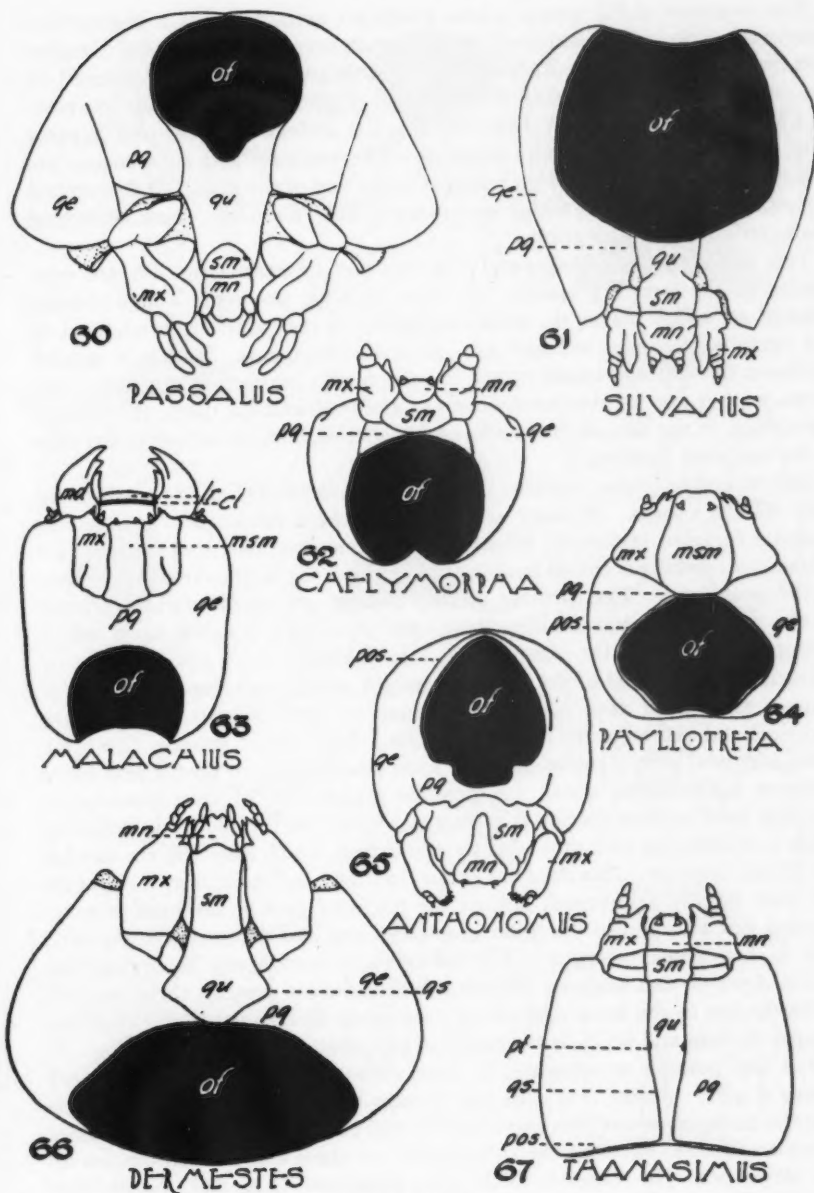
Concerning the head-capsules that are to be considered, it is not difficult to divide them into two groups, namely, those that possess a gula and those that

do not; it is difficult, however, to make further subdivisions owing to the general similarity that exists among many of the species. An effort will be made to group those of different types together, beginning with those that appear to be the more generalized.

The species *Phyllophaga* has already been mentioned in connection with the development of the gular region and there are three other species which resemble this one in respect to the ingrowth of the cervical membrane. *Phyllophaga* and *Osmoderma* (Fig. 52) are very similar, except that the occipital foramen is much larger in the latter. The apodeme is quite extensive in both and it is strengthened by heavily sclerotized crossbars. The only differences appear to be a more complex maxilla in *Osmoderma* and a submentum that is separated from the mentum by a membranous area. *Dorcus* (Fig. 47) and *Allorhina* (Fig. 48) show some similarity in this region and might be placed together, the most notable differences being the apparent absence of a postgenal suture in *Allorhina* and a more extended submentum. Occipital apodemes are present in both species. *Rhyncophorus* (Fig. 46) might also be grouped here as it has some points in common with the others; the ingrown area, however, does not surround the occipital foramen, but extends only over the ventral and part of the lateral margins. An occipital apodeme is present, and the submentum is large, but compared with the surrounding parts of the head-capsule, it is much less heavily sclerotized, the condition being indicated in the figure by slight stippling.

Six species consisting of *Leptinotarsa* (Fig. 56), *Anthonomus* (Fig. 71), *Balaninus* (Fig. 50), *Labidomera* (Fig. 51), *Chelymorpha* (Fig. 62) and *Malachius* (Fig. 63) may be grouped together as having one characteristic in common *i.e.*, the postgenae have grown together forming a bridge of varying width between the occipital foramen and the submentum, and this, together with the tentorial bar, which may be found fused to part of the ental surface, forms a heavily sclerotized plate, adding very considerably to the strengthening and bracing of this area of the head-capsule and resembling very closely the condition found in Lepidoptera. This bridge is quite wide in *Malachius*, *Leptinotarsa* and *Balaninus* and is narrowest in *Chelymorpha*. In all species with the exception of *Malachius*, the submentum shows great development, at the expense, in most cases, of the basal parts of the maxillae and the mentum, which is greatly reduced. In *Malachius* the labium and maxillae show a comparative decrease in size and their situation is more caudad, probably due to the fact that the occipital foramen is more posterior in location. This condition causes the labrum, clypeus and even part of the front, to be considerably anterior to the cephalic margin of the labium and maxillae. The mentum and submentum are apparently fused. The postoccipital area is not well developed in most of the foregoing species, the suture being indiscernible in some. An occipital apodeme occurs in *Balaninus* and *Anisandrus*, the latter also having a frontal apodeme.

Dendroctonus (Fig. 76) might be included here as it somewhat resembles the preceding species. The mentum is well developed, but the submentum, called



FIGS. 60-67.

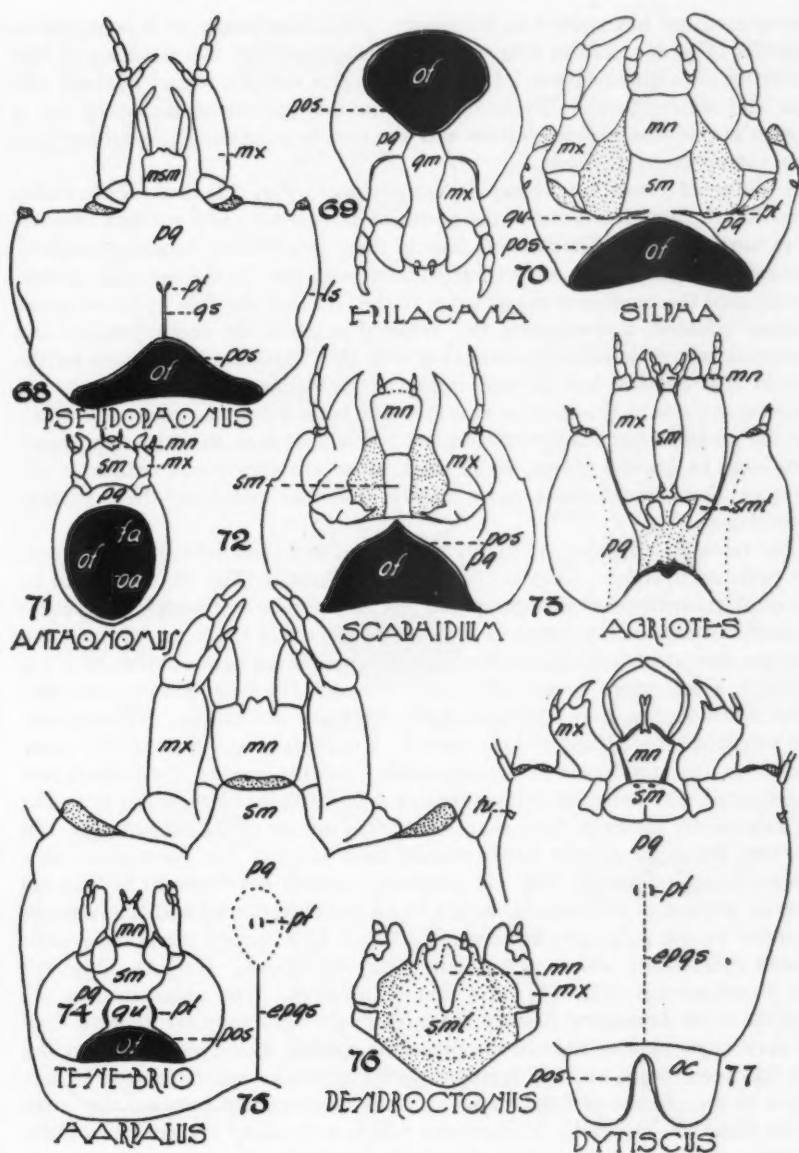
the submental lobe by Hopkins (12), is partly membranous and is separated from the maxillae and the occipital foramen by a membranous area.

The members of the group, whose heads are retracted within the cervical membrane, also have a fusion of the postgenae between the occipital foramen and the submentum. In *Scobicia* (Fig. 57) this area is practically covered by the cervical membrane and in *Acanthocinus* (Fig. 59), it is partially covered. In *Chrysobothris* (Fig. 54), *Xylotrechus* (Fig. 53), *Prionis* (Fig. 58) and *Saperda* (Fig. 55), however, it is fully exposed. The mentum and submentum are distinct in all species, and other than the retraction of the head and the ventral occipital foramen, points which have already been discussed, there is nothing characteristic about this group.

Two other species, *Phyllotreta* (Fig. 64) and *Orchesia* (Fig. 49) are very similar to the foregoing species, but they lack the postgenal bridge already referred to, which makes the posterior margin of the submentum adjacent to the occipital foramen without any gular development. This is a similar structure to what one would expect in such species as *Phyllophaga* and *Osmoderma* were it not for the development of the postoccipital ridge, the cervical membrane, in the case of the two foregoing species, being attached to the edge of the occipital foramen.

Still two other species, *Agriotes* (Fig. 73) and *Lampyris* (Fig. 83) are different from all the others. *Agriotes*, whose head is held horizontally and whose occipital foramen is directly posterior, has a membranous area between the submentum and the occipital foramen and between the most developed portions of the postgenae. The cardines of the maxillae are small sclerotized areas in the membrane, and besides these, are two other isolated areas which Crampton (6) terms the submentales. In addition there are two slightly sclerotized areas joined to the posterior margin, which might be the remains of a more sclerotized area. The submentum is very elongate, likewise the maxillae, and the mentum is quite definite. The second species, *Lampyris*, is not identical with *Agriotes*, but has some resemblance in that it also has a posterior membranous area. A possible explanation of this, however, is that the head of this species is retracted within the prothorax, attached to which is a collar, or fold, only slightly sclerotized, which assists in the mechanism of this function. This does not mean that the head could not be retractile if it were heavily sclerotized, but, as the posterior part of the head is never exposed, but attached to the collar which also acts as a protection, there is no need of heavy sclerotization. The submentum is elongate, somewhat like that in *Agriotes*, and while no definite submentales are present, there is a pair of thickenings in the same position as these areas in *Agriotes* which may correspond to them and which are surrounded by a dotted line in the figure.

It is also possible to separate, to some extent, the species of larvae that possess a gula. *Silpha* (Fig. 70) has already been considered in connection with the development of this region and it will be seen that the gula occupies only a small area, but that the submentum, mentum and prementum are all well developed. In *Tenebrio* (Fig. 75), *Dermestes* (Fig. 66), *Scaphidium* (Fig. 72), *Passalus* (Fig. 60) and *Thanasimus* (Fig. 67), the gula is well developed, being very elongate in the last-mentioned species, with decided evidence



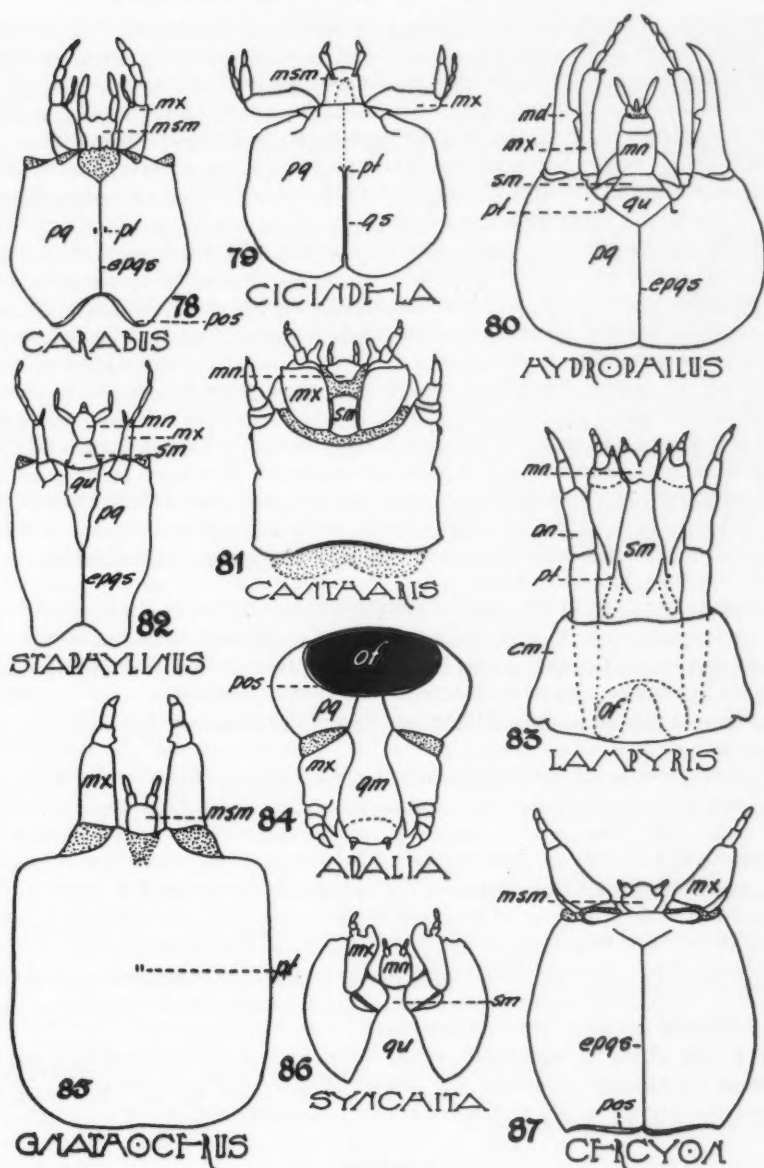
of the tendency of the posterior ends of the gula sutures to become approximated. *Silvanus* (Fig. 61) has a distinct gula, but the suture between it and

the submentum has started to disappear. This disappearance is complete in *Synchlita* (Fig. 86), *Adalia* (Fig. 84) and *Epilachna* (Fig. 69) resulting in the formation of a gulamentum. Gage (8) figures a distinct suture between the gula and submentum in *Epilachna*, but in the specimens examined not a vestige of one was visible, neither was the suture separating the submentum from the mentum apparent.

A different condition occurs in *Staphylinus* (Fig. 82) and *Hydrophilus* (Fig. 80), the approximation of the posterior parts of the gular sutures, referred to as commencing in *Thanasimus*, has, in these two species, become complete, forming a single median suture, called by Crampton (7) the epigular suture. He explains this condition as being due to the fact that the gula in this area has become infolded, and suggests the name of epigulae for those parts of the postgenae which become approximated over it. This area is the more extensive in *Hydrophilus*, but in each instance the visible portion of the gula is situated anterior to the epigular suture. The labium in each species is normal, but the maxillae are worthy of mention. It will be seen that the stipites are very long, as are the galeae, while the laciniae are very much reduced. Altogether these appendages more nearly resemble antennae than gnathal appendages.

The remaining species are highly specialized and it is difficult to interpret the parts accurately. *Cercyon* (Fig. 87) and *Carabus* (Fig. 78) appear to be the most generalized of this group and are very similar. The epigular suture extends throughout the length of the ventral surface of the head, with a small pregular area at its posterior extremity; this is membranous in *Carabus*, which is probably a secondary development and, although the gular sutures are complete in this species, they are beginning to disappear in *Cercyon*. The mentum and submentum are fused in both species. *Cicindela* (Fig. 79) probably comes next from the standpoint of specialization. In this species, the pregula has disappeared, but the gular sutures remain definite as far as the gular pits, and are only faintly indicated from that point to the margin of the submentum. In this case the gular sutures have retained their identity but have practically become fused. *Dytiscus* (Fig. 77) shows still further development in that the anterior portion of the epigular suture has quite disappeared and that portion posterior to the gular pits is very indistinct. This species possesses a well-defined submentum, also a very definite occipital suture. *Harpalus* (Fig. 75) and *Pseudophonus* (Fig. 68) show some similarity. The gular sutures are separate in the latter and fused in the former but, while they are definite, they are very much shorter than in the preceding species, which indicates that the gula has been forced out still further, leaving a greater unbroken area in that region of the ventral surface. There is some development between the bases of the maxillae, especially in *Harpalus* which is possibly the remains of the submentum, although there is no suture separating it from the postgenae.

The greatest specialization occurs in *Cantharis* (Fig. 81) and *Gnathocerus* (Fig. 85), as in these species there is no indication of any gular sutures, the ventral surface being entirely unsegmented. The gular pits were observed in



FIGS. 78 - 87.

Gnathocerus and a small membranous area has developed in the postgenae adjacent to the labium, the maxillae are reduced to a minimum, so that the great degree of specialization gives the ventral surface a very simplified

appearance. The gnathal appendages in *Cantharis* show greater development and give a more generalized appearance, but so far as the fixed parts are concerned, there is little difference between the two species.

Any conclusions that may be drawn from the preceding discussion on the postero-ventral region of the head-capsule must be along the same lines as those given in connection with the fronto-clypeal region, namely, that there is a strong tendency towards the obliteration of sutures and a greater consolidation of parts. It must be borne in mind that there are two distinct types of heads among the species studied, those that have a gula and those that do not. The gradual changes towards specialization, so striking in the former, are not as noticeable in the latter, so far as the postero-ventral region is concerned, as the occipital foramen, in many species, occupies a large area, and the fact that the head is generally shorter does not allow or require much modification. There are, of course, exceptions to this but, as a general rule, the greatest modifications occur where a gula is developing, or where one is disappearing.

It is interesting to note how the gula is believed to develop and then to follow its gradual disappearance, which is fairly completely illustrated in this paper, beginning with the fully developed gula and the gradual drawing together of the gular sutures until they finally meet in an epigular suture, first at the posterior margin and later throughout the entire length of the ventral surface, until the gula has been forced out. Following this, the suture gradually disappears, resulting in the fusion of the postgenae into one solid piece covering the entire ventral surface of the head-capsule. The sclerotization is not as heavy on the ventral surface as it is on the dorsal, but as the sutures disappear, there is naturally a greater compactness, and this, in most cases, corresponds in the different species to the modifications that are at the same time occurring in the fronto-clypeal area.

In some insects, it is believed that certain sclerites force their way in between the base of the labium and the cervical membrane which later develops into the gula. The theory with regard to its formation in the Lepidoptera and Hymenoptera, is that the inner angles of the postgenae become separated, fuse and form the gula. This theory is the one advanced by Stickney (18) with regard to the development of this area in the Coleoptera. He believes that it is formed by the migration of the invaginations of the posterior arms of the tentorium from the occipital foramen towards the submentum, and must therefore be derived from the postgenae. In this migration, are produced the gular sutures, between which is the gula.

The view which Snodgrass (17) takes, however, and which has already been referred to, namely, that the gula originates from the submentum, is more recent and the one which finds most favor at the present time.

Summary

1. Only a limited amount of work has been done on the comparative anatomy of the head-capsules of coleopterous larvae.
2. A very wide variation of structure occurs among the species studied.

3. This variation ranges from a very generalized condition in such species as *Phyllophaga*, to a condition showing great specialization, as in the genus *Gnathocerus* and others. Whatever the degree of specialization, however, there is no relation between it and the condition found in the adults.

4. Antennae were present in all species with the exception of *Rhyncophorus*. They were comparatively long and conspicuous in some species and very minute in others.

5. Ocelli may be present or absent and differ both in number and position.

6. As a general rule, the more generalized condition was found among the eruciform type of larvae.

7. Among the campodeiform species the greatest specialization occurs. This is, in some measure, due to the fact that the head is held in a more or less horizontal position.

8. The general trend of specialization is towards the obliteration of sutures and a greater compactness and consolidation of the head-capsule.

9. Coincident with loss of sutures there is a tendency towards greater sclerotization.

10. While other conditions undoubtedly occur among species that have not been studied, they would come within the two extremes of structure found among species dealt with in this paper.

Acknowledgments

The writer wishes to express his appreciation to Dr. E. Melville DuPorte of Macdonald College for his instruction and for his criticisms and suggestions during the course of this work. He also wishes to thank Dr. G.W. Underhill of the Virginia Agricultural Experiment Station, for providing him with specimens of *Epilachna borealis*, Dr. A. W. Rymer Roberts of the Molteno Institute, for representatives of the families Staphylinidae and Cantharidae, and Dr. C. W. Collins of the U. S. Bureau of Entomology, for specimens in the genera *Calosoma* and *Carabus*.

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A NEW SPECIES OF PHOMOPSIS¹

BY H. T. GÜSSOW² AND W. R. FOSTER³

Abstract

In the fall of 1930, both authors independently isolated the identical fungus from lesions of a characteristic stem-end hard rot of potatoes. The fungus belongs to the genus *Phomopsis* and as it is materially distinct from any known species in details of artificial and natural growth, it is proposed to establish it as a new species. The authors further collaborated in studying the taxonomy of the fungus. A description of the disease caused by this organism and the results obtained from a study of its pathogenicity and physiology will be published at a later date.

Morphology of Fungus

Pycnidia (Figs. 1, 2, 5) within a stroma; mature stroma prominent, innate at first, later erumpent, $0.25-0.50 \times 1-2$ mm. in size; dothideoid, sessile; broad base, cushion to variable in shape; single, occasionally confluent; sclerotial. At first like a typical sclerotium; coal black, rough externally, soft to cartilaginous, not brittle, easily sectioned; interior: macroscopically black; microscopically towards apex with series of dark-colored thick walled cells, towards base these are fewer. Substance hyaline, cellular. When spore formation takes place upper portion of stroma dividing into several irregular ridge-like, separate cavities; as absorption takes place forming into one cavity, very irregular and typically dothideoid. Hymenium lining entire walls of cavity. Towards hymenium the hyaline color changes into a pale fuscous tint. Finally more or less indistinctly papillate. Papillae modestly beaked and developed anywhere over the surface of the stroma. Cavities filled with conidia, later discharging through ostiole in form of milky white bead, (Fig. 5) "A" spores (of Diedicke's) shown in Fig. 4.

Conidia (Figs. 3, 4 and 5) length $10.72 \pm 0.96 \mu$, modal length 11.85μ , minimum length 7.11μ , and maximum length 13.03μ , width $4-6 \mu$, hyaline, one-celled, spindle shaped, guttulate. Conidiophores (Fig. 5A) prominent persistent, subulate, septate at base, $15-18 \times 1.5 \mu$, simple. Stylospores were found only on two occasions, once on a diseased lesion of the tuber and once in a culture on cooked barley seed. These spores, which resemble the "B" spores of Diedicke, were filiform, curved or straight, and measured $8-30 \times 0.5-1.5 \mu$ (Fig. 5 C).

Type on leaves and tubers of *Solanum tuberosum* L. Vancouver, British Columbia, October, 1930, Coll. H. S. MacLeod, District Plant Disease Inspector, Division of Botany, Dominion Department of Agriculture.

Phomopsis tuberivora Güssow et Foster. sp.n.

Pycnidiis in stromate immersis; stromate maturo conspicuo, $0.25-0.50 \times 1-2$ mill., dothidioido, sessili, base lata, forma variabili, nigro, singulari, nonnunquam confluenta, sclerotioideo.

¹ Manuscript received February 24, 1932.

Contribution from the Division of Botany, Experimental Farms, Ottawa, and the Provincial Plant Laboratories, British Columbia.

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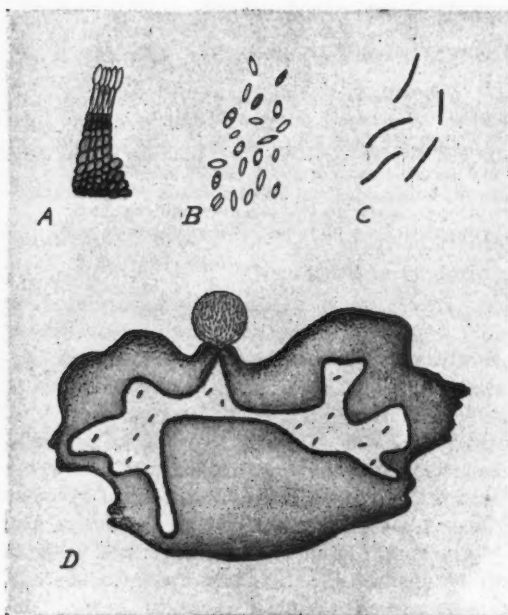


FIG. 5. Camera lucida drawings: A—Conidiophores bearing conidia, "A" spores. B—Conidia, "A" spores. C—Stylospores, "B" spores. D—Cross section of pycnidium, conidia discharge through ostiole in milky white bead "A" spores.

Conidiis, 1-cellularibus, hyalinis, fusiformibus, guttulis; $10.72 \pm 0.96 \mu \times 4-6 \mu$.

Conidiophoris prominentibus, non deciduis, subulatis, basibus septatis, $15-18 \mu \times 1.5 \mu$, simplicibus.

Stylosporis, 1-cellularibus, filiformibus, curvatis vel rectis, $8-30 \mu \times 0.5-1.5 \mu$.

Hab. in foliis et tuberculis *Solani tuberosi* L., Vancouver, Columbia Britannica, America borealis.

Discussion

W. B. Grove (2, p. 68) described a new species of *Phomopsis* found by A. D. Cotton on dead stems of *Solanum tuberosum* in Hampshire, England, to which he gives the specific designation, *P. solani*. In general generic characters our fungus agrees with that of Grove's. The fruiting bodies, however, of our species, are up to 2 mm. long, 1 mm. broad and $\frac{1}{2}$ -1 mm. in depth. Further, the spores measure almost double that given by Grove and are frequently multi guttulate. The conidiophores of *Phomopsis solani* are $10-15 \mu$, whereas in our specimen they were $15-18 \mu$ in length. Furthermore it was isolated from living specimens of tubers of *Solanum tuberosum*, collected from several districts of British Columbia. None of the other species agree even remotely with this fungus, we therefore propose to name it *Phomopsis tuberivora*, Güssow et Foster, sp. n.

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FIG. 1. Pycnidia of *Phomopsis tuberivora* developing on lesion of potato tuber. (Photo J. B. McCurry.)

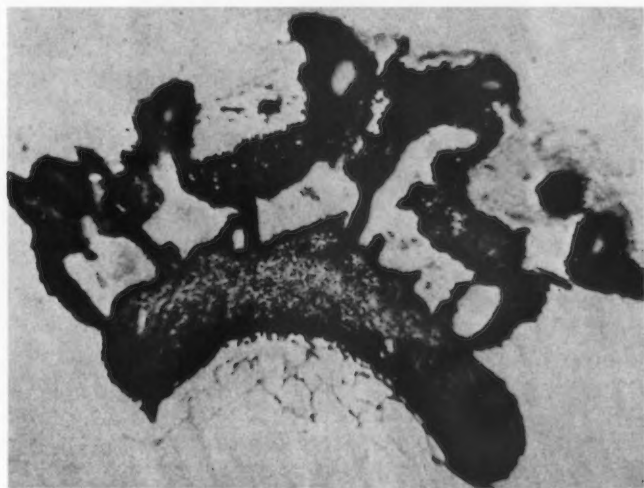


FIG. 2. Photomicrograph of cross section of pycnidium of *Phomopsis tuberivora*. $\times 60$.



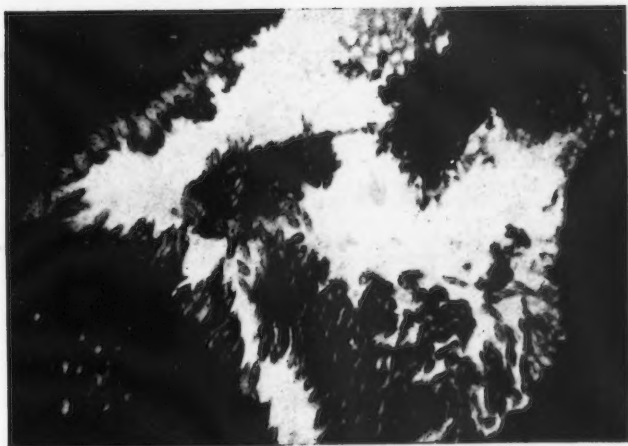


FIG. 3. Photomicrograph of conidia within a cavity of the pycnidium of *Phomopsis tuberivora*. $\times 400$.

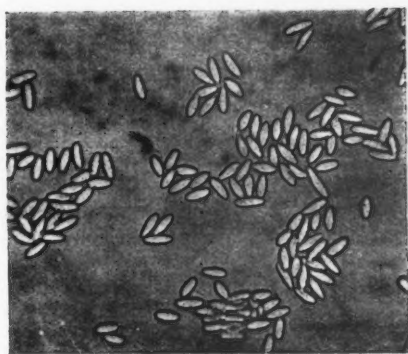


FIG. 4. Photomicrograph of conidia, "A" spores of *Phomopsis tuberivora*. $\times 400$.



REACTION OF FLOUR OF SOME VARIETIES OF HARD RED SPRING WHEAT TO BLEACHING AGENTS¹

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Abstract

Composite samples of "aged" flour of 17 varieties of spring wheat grown in western Canada, were bleached by three methods, namely, $\frac{3}{4}$ oz. Betachlor per bbl., 1 lb. Novadel per 40 bbl., and $\frac{3}{4}$ oz. Betachlor per bbl. followed by 1 lb. Novadel per 40 bbl. Gasoline color values were determined for the bleached and unbleached samples and it was found that the more highly pigmented flours in the series could be reduced to approximately the same color as the less pigmented samples, indicating that the former respond to a greater extent to bleaching than the latter. The color of the bread was improved in all cases, the greatest improvement occurring with Betachlor plus Novadel and the least with Betachlor alone. Loaf volumes obtained with six different baking formulas showed no significant difference between bleached and unbleached samples. None of the dosages showed any evidence of overbleaching. It was thought that information might be obtained on the relative susceptibility of the varieties to damage by bleaching agents, but it was found that normal dosages are not sufficient for differentiation on this basis. It is suggested that this might be accomplished by using heavier dosages of Betachlor.

In the domestic trade, flour color and the ease or difficulty of reducing it by bleaching are important factors in the evaluation of varieties. One of the first objections raised by Canadian millers against Garnet wheat was that it produces a yellow flour that cannot be bleached satisfactorily. Other varieties, notably Parker's Selection and Marquillo, have been discriminated against for the same reason. There are available many good varieties of hard red spring wheat of satisfactory agronomic characteristics and hence it is not surprising that any new introduction may be condemned if it fails to compare favorably with the standard variety, Marquis, on even a single count. It is necessary, therefore, when making comparative studies of varieties of one class to consider flour color and reaction to bleaching as well as the baking strength. Malloch, Geddes, and Larmour (8) have conducted an extensive comparative study of the milling and baking quality of the principal varieties grown in western Canada. As residues of the flours used in that study were available it was thought advisable to conduct a special investigation of flour color, bleaching, and the effect of bleaching agents on loaf volume.

Materials

There were available from the 1929 Variety series (8) certain flour residues from which were chosen 17 varieties, each grown in 10 different places. The 10 samples of each variety were thoroughly mixed, giving 17 composite flours each containing aliquots representing the same 10 places of origin. Larmour

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and Brockington (6) have shown that composites made of samples of one variety from different places give results in good agreement with the average values obtained from the tests of the individuals. It was considered, therefore, that the composites would give a very fair estimate of the general reaction of the varieties for study. The varieties were Kitchener, Preston, Red Fife, Dicklow, Garnet, Red Bobs 222, Reward, Marquis, Marquillo, Hard Federation, Early Triumph, Axminster, Renfrew, Supreme, Huron, Kota, and Parker's Selection. They were grown in Edmonton, Lethbridge, Lacombe, Swift Current, Indian Head, Rosthern, Saskatoon, Scott, Winnipeg and Brandon. After being thoroughly mixed, the flours were subdivided into three parts, one of which was sent to each of the collaborating laboratories, where they were halved, one-half being retained as a check sample and the other being bleached. The bleaching methods used in the different laboratories were:— Laboratory A; Novadel at the rate of 1 lb. per 40 bbl.; Laboratory B, Betachlor at the rate of $\frac{3}{4}$ oz. per bbl.; Laboratory C, Betachlor $\frac{1}{2}$ oz. per bbl. followed by Novadel at the rate of 1 lb. per 40 bbl. Color of the bleached and unbleached samples was estimated by the tentative method of the Association of Official Agricultural Chemists (1, p. 176), using high grade gasoline for the extraction. Comparisons were made against a 0.005% solution of potassium chromate in a suitable colorimeter.

The advantages of this method of estimating color are that it is rapid and requires no intricate or expensive apparatus. It has the disadvantage that the reference color standard consisting of 0.005% potassium chromate is not entirely satisfactory inasmuch as the hue does not exactly match the hue of a gasoline solution of carotin. Jorgensen (4), Kent-Jones and Herd (5), and Visser't Hooft and de Leeuw (9) have suggested various modifications of the color standard, but none of these have proved entirely suitable. Use of a color analyzer has been shown by Ferrari and Bailey (3) to give the best results but the spectrophotometers on the market at present are exceedingly expensive and no such apparatus is available in any of the collaborating laboratories. As this is merely a preliminary study of color it was decided, therefore, to use the chromate standard in order to ascertain if the results obtained would warrant a more thorough investigation of this phase of flour testing.

In dealing with the effects of bleaching agents, a very useful figure is obtained by calculating the ratio of the gasoline color values of the bleached and unbleached flours. This ratio gives a convenient measure of the reduction in color and is valuable in comparing the effectiveness of various bleaching materials and also in comparing the response of different varieties or samples to the same bleaching agent. The ratio of the bleached and check samples can be determined also directly in the colorimeter by using one of the extracts in place of the chromate color standard. This procedure has the advantage that the colors vary only in intensity and should therefore obviate errors attributable to difficulties in matching the chromate standard. The usefulness of such values is strictly limited as they give no indication of the actual color value of the flour, but represent only the relative changes in color intensity.

However, if the ratios obtained by these two different methods agree, one may assume that the error due to matching of hues is not large. A comparison of these ratios was made in two of the laboratories and the results in Table I

TABLE I
RATIOS BLEACHED TO UNBLEACHED COLOR VALUES DETERMINED BY CALCULATION FROM THE SEPARATE GASOLINE COLOR VALUES AND BY COMPARING THE TWO EXTRACTS DIRECTLY IN THE COLORIMETER

Variety	Gas. color value (against K_2CrO_4)		Ratio B/C calculated	Ratio B/C det'm'd. directly	Gas. color value		Ratio B/C calculated	Ratio B/C det'm'd. directly
	Check	Bleached (Nov. + Cl_2)			Check	Bleached (Betachlor)		
1. Kitchener	1.54	0.50	0.33	0.35	1.52	0.96	0.63	0.68
2. Preston	1.52	0.45	0.30	0.28	1.01	0.86	0.86	0.82
3. Red Fife	1.25	0.50	0.40	0.44	1.36	1.10	0.81	0.83
4. Dicklow	1.22	0.34	0.28	0.38	1.62	1.52	0.94	0.89
5. Garnet	1.25	0.47	0.38	0.38	1.21	1.12	0.92	0.88
6. Red Bobs	1.10	0.31	0.28	0.31	1.43	1.16	0.81	0.77
7. Reward	1.03	0.40	0.39	0.35	1.32	1.06	0.80	0.75
8. Marquis	1.10	0.36	0.33	0.35	1.27	1.15	0.90	0.81
9. Marquillo	1.67	0.49	0.29	0.31	0.95	0.78	0.82	0.81
10. Hd. Federation	1.10	0.35	0.32	0.34	1.22	1.15	0.94	0.77
11. Early Triumph	1.10	0.35	0.32	0.31	1.17	1.06	0.91	0.85
12. Axminster	1.76	0.46	0.26	0.30	0.78	0.67	0.86	0.83
13. Renfrew	1.34	0.49	0.37	0.40	1.11	1.01	0.91	0.79
14. Supreme	1.25	0.35	0.28	0.31	1.01	1.01	1.00	0.90
15. Huron	1.76	0.32	0.18	0.15	1.07	0.86	0.80	0.72
16. Kota	1.08	0.33	0.30	0.30	1.10	1.07	0.97	0.74
17. Parker's Sel.	2.00	0.42	0.21	0.18	0.79	0.78	0.99	0.88
Average			0.31	0.32			0.87	0.81

show that they agree quite well. The data of Laboratory C have as means 0.31 and 0.32 for the calculated and observed ratios; Laboratory B gave data with means 0.87 and 0.81. With few exceptions, the differences between ratios obtained in both ways show a range of 5-10%. Evidently the error involved in use of the chromate standard is not unduly large.

Effect of the Different Bleaching Agents

In considering the effect of the different bleachings on these flours it should be borne in mind that the flours were already well aged and presumably had undergone considerable reduction in color before the chemical bleaching agents were applied. No work has been done on the effect of natural aging on the response of flour to chemical bleaching agents and it cannot be said therefore whether the percentage reduction in color noted in this series is greater, equal, or less than would be obtained by treating freshly milled flours.

The best estimate of the color of the unbleached check samples is the average of the determinations made in the three laboratories. The bleached samples, however, were different in each laboratory, as a different bleaching method was used in each. If the colors of the bleached samples were compared with the

average value for the check samples, certain discrepancies would occur because of slight differences in technique. Therefore, in order to use the average color value of the check samples it is necessary to recalculate the value for the bleached samples. This is readily done by use of the ratio bleached to unbleached which was determined for the data of each laboratory. Table II

TABLE II
GASOLINE COLOR VALUES OF UNBLEACHED SAMPLES AND OF SAMPLES BLEACHED
IN THREE DIFFERENT WAYS

Variety	Av. gas. color value unbleached	Betachlor, ½ oz. per bbl.		Novadel, 1 lb. 40 bbl.		Betachlor, ½ oz. per bbl. + Novadel, 1 lb. per 40 bbl.	
		Gas. color value	Ratio B/C	Gas. color value	Ratio B/C	Gas. color value	Ratio B/C
1. Kitchener	1.32	0.83	0.63	0.74	0.56	0.43	0.33
2. Preston	1.18	1.01	0.86	0.59	0.50	0.35	0.30
3. Red Fife	1.17	0.95	0.81	0.51	0.44	0.47	0.40
4. Dicklow	1.15	1.08	0.94	0.58	0.50	0.32	0.28
5. Garnet	1.09	1.00	0.92	0.67	0.62	0.41	0.38
6. Red Bobs	1.11	0.90	0.81	0.56	0.50	0.31	0.28
7. Reward	1.05	0.84	0.80	0.52	0.50	0.41	0.39
8. Marquis	1.06	0.95	0.90	0.53	0.50	0.35	0.33
9. Marquillo	1.24	1.02	0.82	0.67	0.54	0.36	0.29
10. Hd. Federation	1.01	0.95	0.94	0.43	0.43	0.32	0.32
11. Early Triumph	1.02	0.93	0.91	0.39	0.38	0.33	0.32
12. Axminster	1.28	1.10	0.86	0.40	0.31	0.33	0.26
13. Renfrew	1.08	0.98	0.91	0.54	0.50	0.40	0.37
14. Supreme	1.09	1.09	1.00	0.55	0.50	0.30	0.28
15. Huron	1.28	1.02	0.80	0.64	0.50	0.23	0.18
16. Kota	0.99	0.96	0.97	0.38	0.38	0.30	0.30
17. Parker's Selection	1.36	1.35	0.99	0.63	0.46	0.29	0.21
Average			0.87		0.48		0.31

shows the data calculated in this way on the basis of the mean of the check samples. The average reduction in color effected by the three bleaches was: Betachlor, 13%; Novadel, 52%; Betachlor followed by Novadel, 69%. It is of interest to note that with the combination of Betachlor and Novadel the final color values were very similar, indicating that generally the more highly pigmented flours react to a relatively greater extent than the less highly pigmented flours. Thus the very yellow Parker's Selection with an original color value of 1.36 bleaches down to 0.21, a reduction of 79%, while the light colored Kota of color 0.99 is reduced in color 70% to a value of 0.30. A large reduction of intensity is found in all the highly pigmented flours, namely, Kitchener, Marquillo, Axminster, and Huron, and confirms an observation previously made by one of us* that in the flour of Marquillo-Marquis crosses, those samples carrying heavy color are bleached to a greater degree than the less heavily colored samples in the same treatment. This is a very interesting observation and one that if conclusively proved would have an important bearing on the

*Private communication.

problems of plant breeders engaged in the production of improved varieties of wheat. In the past considerable emphasis has been laid on color and doubtless selections which were otherwise promising have been discarded on this account. In testing new strains and selections it would be advisable, therefore, to study the reaction to bleaching agents rather than only the color of the unbleached sample.

The results so far considered show that by use of either Novadel, or a combination of Betachlor and Novadel, the yellow color of the flour of any of the varieties studied can be satisfactorily reduced. It frequently occurs, however, that bleaching which is too severe has a bad effect on the bread color, producing, in place of the objectionable yellow tint, a more objectionable grey, or in some cases, a pale pasty color. An examination of the crumb color scores assigned in the various bakings should give an estimate of whether or not such changes had occurred as a result of the bleaching.

It is deplorable that the scoring of bread color still remains a matter of personal judgment of the baker, as no adequate apparatus or procedure for obtaining a more accurate estimate has been developed. However, it may be said that an experienced baker in any given laboratory will have a nicely adjusted scale of color values that may be relied upon to give fairly accurate relative results for scores made in that laboratory. The three collaborating laboratories have attempted to standardize color scoring of bread by using a common standard flour, and by comparing from time to time scores made on different samples of bread. The color scores are designated by numbers as follows:— 8, creamy yellow or dull white; 7, yellow; 6, dull yellow or very slightly grey; 5, very yellow or slightly grey; 4, greyish yellow; 3, dull grey; 2, very grey; 1, greyish brown. "Creamy yellow" is considered two points better than "very slightly grey", while "very yellow" is three points better than "very grey". Therefore, if an unbleached flour gave yellow bread, any hint of grey in the bread from bleached flour would result in a reduction of color score. With these points in mind, the bread color scores found with four baking formulas may be examined to see how the changes effected by bleaching the flour are manifested in the baking results.

Considering first the flours bleached with Betachlor only, the results in Table III indicate that no appreciable change in bread color occurred. The improvement in bread color by Novadel and Betachlor-Novadel bleaching is shown in Tables IV and V by the actual and percentage increases in color scores. Novadel bleaching (Table IV) gave an increase of one or more points in all samples except 10 and 14 (0.001% bromate baking). In these data there is no suggestion whatever of damage to color, but on the contrary every evidence of marked improvement. The samples bleached with Betachlor plus Novadel showed generally a greater improvement in bread color than the Novadel bleached samples. It can be seen from Table V that there was in no case, by any of the baking formulas applied, any decrease but rather a very distinct improvement in crumb color. It appears evident that all these varieties can be bleached satisfactorily from the standpoint of both flour color

and bread color and it is doubtful, therefore, that they can be differentiated by this means.

TABLE III

IMPROVEMENT IN CRUMB COLOR OF THE BREAD DUE TO BLEACHING WITH BETACHLOR ONLY.
EXPRESSED IN ACTUAL POINTS AND IN PERCENTAGES

Variety	Improvement in crumb color of bleached samples							
	Simple		Bromate (0.001%)		Blend- bromate		Diastatic malt and phosphate	
	Points	%	Points	%	Points	%	Points	%
1. Kitchener	1.5	25	0	0	1.0	14	1.0	14
2. Preston	0.5	8	0	0	0.5	7	0.5	7
3. Red Fife	1.0	17	0	0	0.1	14	0.5	7
4. Dicklow	1.5	25	0	0	0.5	7	0.5	7
5. Garnet	0.0	0	0.5	7	0.5	7	0.0	0
6. Red Bobs	1.0	17	0.5	6	0.0	0	1.0	14
7. Reward	1.0	17	0.0	0	0.0	0	1.0	14
8. Marquis	0.5	8	0.0	0	0.0	0	-0.5	-7
9. Marquillo	0.0	0	-0.5	-6	0.0	0	-0.5	-8
10. Hd. Federation	0.0	0	0.5	6	0.0	0	0.5	7
11. Early Triumph	0.0	0	0.5	6	0.0	0	0.0	0
12. Axminster	0.5	8	0.5	7	0.5	7	0.5	7
13. Renfrew	0.0	0	0.5	7	0.0	0	0.0	0
14. Supreme	0.0	0	0.0	0	0.0	0	0.5	7
15. Huron	-0.5	-8	0.0	0	0.0	0	0.0	0
16. Kota	0.0	0	0.0	0	0.0	0	-0.5	-7
17. Parker's Sel.	0.0	0	0.0	0	-0.5	-6	0.0	0

TABLE IV

IMPROVEMENT IN CRUMB COLOR OF THE BREAD DUE TO BLEACHING WITH NOVADEL.
EXPRESSED IN ACTUAL POINTS AND IN PERCENTAGES

Variety	Improvement in crumb color of bleached samples											
	Simple		Bromate (0.001%)		Bromate (0.002%)		Blend- bromate		Malt- arkady		Diamalt & phosphate	
	Points	%	Points	%	Points	%	Points	%	Points	%	Points	%
1. Kitchener	2	33	2	33	2	33	2	29	1.5	25	2	33
2. Preston	2	33	2	33	3	50	1	14	1.5	25	2	33
3. Red Fife	2	33	1.5	20	2	33	2	29	1.5	25	2	33
4. Dicklow	2	33	1	14	1	14	1.5	20	2	33	2	33
5. Garnet	1	17	1	14	2	33	3	50	1	18	1	17
6. Red Bobs	1	14	1.5	20	3	50	2	29	1	15	1	14
7. Reward	2	29	1.5	20	2	29	1.5	20	2	31	2	29
8. Marquis	2	33	1.5	20	1	14	2	29	2	36	2	33
9. Marquillo	2	40	1.5	25	3	60	1.5	25	2	40	2	40
10. Hd. Federation	2	29	0.5	7	3	50	2	29	2	31	2	29
11. Early Triumph	3	50	2	29	3	50	2	29	3	54	3	50
12. Axminster	2.5	45	1	17	3	60	3	50	1.5	50	2.5	45
13. Renfrew	1	14	1.5	20	1	14	2	29	1.5	25	1	14
14. Supreme	3.5	64	0.5	7	1	14	2	29	3.5	70	3.5	64
15. Huron	2.5	45	2	33	2	29	2	29	2.5	50	2.5	45
16. Kota	2.5	45	1	14	2	33	2	29	2.5	50	2.5	45
17. Parker's Sel.	2	40	1.5	50	3	60	1.5	25	2	40	1.5	27

TABLE V

IMPROVEMENT IN CRUMB COLOR OF THE BREAD DUE TO BLEACHING WITH BETACHLOR FOLLOWED BY NOVADEL. EXPRESSED IN ACTUAL POINTS AND IN PERCENTAGES

Variety	Improvement in crumb color of bleached samples											
	Simple		Bromate (0.001%)		Bromate (0.002%)		Blend-bromate		Malt-arkady		Diamalt & phosphate	
	Points	%	Points	%	Points	%	Points	%	Points	%	Points	%
1. Kitchener	3	50	1.5	20	2	27	1.5	20	2	29	2.5	38
2. Preston	4	80	3	46	2	29	2.5	36	1.5	21	3	54
3. Red Fife	4	67	2	27	1.5	18	1.5	18	2.5	33	2	29
4. Dicklow	2	29	1.5	19	1	12	0.5	6	1	14	2	29
5. Garnet	3	50	1.5	20	2	29	1	12	0.5	9	2	33
6. Red Bobs	3.5	54	2.5	33	2	25	1	11	1.5	19	2	29
7. Reward	1.5	20	1.5	18	2	25	1.5	18	2	33	2	29
8. Marquis	2.5	36	2	25	3	40	1	11	2	29	1.5	21
9. Marquillo	3.5	78	2.5	6	2.5	36	2.5	36	3	50	3	60
10. Hd. Federation	2	29	2	27	2	25	2	25	2	29	2	29
11. Early Triumph	2	31	2	25	2.5	33	2	25	2	29	3	50
12. Axminster	3.5	70	2.5	36	3.5	58	3	43	3	60	4	80
13. Renfrew	1.5	21	1.5	17	2	25	1	11	2	29	2	29
14. Supreme	2.5	42	2	25	3	43	1.5	18	2	29	2	29
15. Huron	2	40	2.5	36	2.5	36	1.5	19	3	50	2	17
16. Kota	1.5	27	2	29	2.5	33	1.5	18	2	29	1.5	27
17. Parker's Sel.	2.5	50	3.5	64	2.5	38	2.5	38	3	60	1.5	30

Effect of Bleaching on Loaf Volume

Bleaching agents that contain chlorine have, in addition to their effect on color, an aging effect on flour. An overdosage of the bleaching agent will injure the baking quality. This type of damage is known as "overbleaching". Larmour and Machon (7) have shown that this effect is related to protein content and loaf volume of the flour, and that flours very low in protein are more readily overbleached than the average of high protein flours. Overbleaching can usually be detected most readily by use of formulas involving oxidizing agents because, if the bleaching has modified the flour to its limit, further action of powerful oxidizers will cause it to break in strength, thus producing lower loaf volumes than are obtained when the unbleached flour is baked in the same way. Thus the simple and malt-phosphate formulas are useful in estimating the extent to which maturation has progressed, while the bromate, blend-bromate, and malt-arkady formulas will expose any weakness occasioned by carrying the maturation process too close to the limit of strength of the flours. Malloch, Geddes, and Larmour (8) have shown that in these varieties there are real differences in strength, as judged by the baking data. The authors were interested in ascertaining if their behavior after bleaching would reveal further qualitative differences.

For convenience in tabulating the data, the loaf volume of the bleached sample has been calculated as percentage of the corresponding unbleached samples and for each variety the averages of the simple and malt-phosphate

data, and of the data from formulas involving an oxidizer have been computed. The results are given in Tables VI, VII, and VIII.

TABLE VI
LOAF VOLUME OF BLEACHED SAMPLES AS PERCENTAGE OF LOAF VOLUME OF
CHECK SAMPLES (BETACHLOR BLEACH)

Variety	Simple	Bromate (0.001%)	Blend- bromate	Diastatic malt and phosphate	Mean simple and malt phosphate	Mean bromate and blend- bromate
1. Kitchener	105	92	92	112	108.5	92
2. Preston	107	97	101	106	106.5	99
3. Red Fife	105	93	95	104	104.5	94
4. Dicklow	101	104	96	110	105.5	100
5. Garnet	99	92	102	102	100.5	97
6. Red Bobs	104	99	101	102	103	100
7. Reward	108	98	105	106	107	101
8. Marquis	102	107	97	100	101	102
9. Marquillo	104	111	102	100	102	106.5
10. Hd. Federation	102	104	103	102	102	103.5
11. Early Triumph	99	102	103	103	101	102.5
12. Axminster	97	104	101	98	97.5	102.5
13. Renfrew	101	97	105	102	101.5	101
14. Supreme	99	112	108	97	98	110
15. Huron	104	91	104	99	101.5	97.5
16. Kota	102	104	99	104	103	101.5
17. Parker's Sel.	97	98	128	94	95.5	113.5
Mean	102	100.3	102.7	102.4		

TABLE VII
LOAF VOLUME OF BLEACHED AS PERCENTAGE OF LOAF VOLUME OF CHECK SAMPLES
(NOVADEL BLEACH)

Variety	Simple	Bromate (0.001%)	Bromate (0.002%)	Blend- bromate	Malt- arkady	Diastatic malt and phosphate	Mean
1. Kitchener	102	101	101	97	101	102	0.5
2. Preston	102	98	101	101	106	97	1.0
3. Red Fife	99	100	104	97	101	101	0
4. Dicklow	102	99	98	101	101	106	1
5. Garnet	103	106	102	100	99	100	1.5
6. Red Bobs	101	94	97	97	96	98	-3
7. Reward	102	103	101	100	101	103	1.5
8. Marquis	102	99	100	102	99	98	0
9. Marquillo	100	98	101	99	96	98	-1
10. Hd. Federation	100	101	97	97	103	101	0
11. Early Triumph	103	102	99	98	97	100	0
12. Axminster	98	95	99	98	103	94	-2
13. Renfrew	98	103	103	100	101	100	1
14. Supreme	99	101	101	98	102	103	0.5
15. Huron	98	101	101	100	102	101	0.5
16. Kota	100	101	101	102	101	98	0.5
17. Parker's Sel.	101	99	102	102	98	100	0.5
Mean	100.6	100	100.5	99.4	100.4	100	

TABLE VIII
LOAF VOLUME OF BLEACHED AS PERCENTAGE OF CHECK SAMPLES
(BETACHLOR PLUS NOVADEL BLEACH)

Variety	Simple	Bromate (0.001%)	Bromate (0.002%)	Blend- bromate	Malt- arkady	Malt- phos- phate	Mean, simple and malt- phosphate	Mean of oxidizer formulas
1. Kitchener	104	96	96	101	100	104	104	98.2
2. Preston	110	94	98	102	99	109	109.5	98.2
3. Red Fife	105	100	95	98	103	106	105.5	98.8
4. Dicklow	102	106	101	95	94	100	101	97.5
5. Garnet	102	98	98	102	102	107	104.5	100
6. Red Bobs	105	97	100	100	101	106	105.5	99.5
7. Reward	105	93	95	99	101	105	105	97
8. Marquis	104	89	95	104	96	105	104.5	96
9. Marquillo	106	98	101	98	104	104	105	100.2
10. Hd. Federation	105	95	93	100	98	103	104	96.5
11. Early Triumph	106	98	93	100	97	104	105	97
12. Axminster	104	94	95	103	98	103	103.5	97.5
13. Renfrew	106	95	96	99	94	101	103.5	96
14. Supreme	102	100	97	97	96	103	102.5	97
15. Huron	101	98	99	101	95	109	105	98.2
16. Kota	100	102	97	96	97	103	101.5	98
17. Parker's Sel.	103	99	99	103	98	105	104	99.8
Mean	104	97	97	100	98	104.5		

The data with the Betachlor bleach, in Table VI, show that some maturing occurred in all varieties except Axminster, Supreme and Parker's Selection. These three gave loaf volumes slightly below the checks by the simple and malt-phosphate formulas, but as they all showed an increase by the bromate formulas the differences noted cannot be considered significant. When baked by the bromate formulas, Kitchener, Red Fife, Garnet, and Huron gave a decrease which is probably significant only in the first two. On the whole it may be concluded that the Betachlor bleach improved the loaf volume without causing any weakness except possibly in Kitchener and Red Fife.

Novadel alone is reputed to have little or no effect in respect to maturing and it is not surprising, therefore, that the data in Table VII show no differences that may be considered significant.

Table VIII shows that in practically all cases the double bleaching with Betachlor plus Novadel resulted in increased loaf volume when the samples were baked by the simple and malt-phosphate formulas. With the bromate formulas there was generally a slight, perhaps non-significant, decrease in loaf volume. The greatest decrease noted was 11% with Marquis in the 0.001% bromate baking. The varieties showing the greatest decreases in the average of the four bromate formulas were: Marquis and Renfrew each, 4%; Hard Federation, 3.5%; Reward, Early Triumph and Supreme each, 3%.

This examination of the loaf volume data indicates that all these varieties were satisfactorily bleached, that no appreciable overbleaching occurred, and that the chlorine bleaches produced a slight degree of maturing

despite the fact that the flours were all quite well aged before bleaching. Application of normal dosages of these two bleaching agents alone or in combination produced no depreciation of quality in any of the 17 varieties studied and this method, therefore, provided no means for differentiating them in respect to strength. In order to serve this purpose it is likely that abnormal dosages would have to be applied as in the study made by Larmour and Machon (7). It would be necessary to select a dosage of a chlorine bleach that would mature an average or standard variety to its limit and observe what varieties were damaged by this treatment. This would be of scientific interest but of no practical significance as a test method, because more rapidly applied tests of strength are available.

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THE KINETICS OF THE OXIDATION OF GASEOUS ACETONE¹

By E. W. R. STEACIE²

Abstract

The oxidation of gaseous acetone is a homogeneous chain reaction between 350° and 500° C. The effect of pressure on the rate of the reaction indicates an "order" somewhat greater than three. The indications are that the first step in the reaction consists of the formation of an unstable peroxide. The predominant reaction then appears to be the formation of acetic and formic acids together with their products of oxidation and decomposition. The actual course of the reaction varies somewhat as the temperature changes.

The temperature coefficient and the effects of surface and of foreign gases show that the chain length is comparatively short and varies with temperature. The process by which the chains are initiated is probably bimolecular. The reaction differs from most oxidation reactions of the chain type in that the concentrations of the two reactants are about equally important in so far as their effect on the rate of the reaction is concerned.

Introduction

The idea of reaction chains was originally put forward to explain those photochemical reactions in which more than one molecule reacts per quantum of light absorbed. Recently, however, it has been shown that certain thermal reactions may occur by a chain mechanism. In such cases the first step is a reaction of an ordinary bimolecular or termolecular type. This gives rise to a product molecule endowed with excess energy (the heat of activation plus the heat of reaction). This activated product molecule then activates a fresh molecule of the reactant by collision, and so on, a reaction chain being produced. This reaction chain is finally broken by the deactivation of a molecule either in the gas or at the wall of the containing vessel.

It is obvious that a mechanism of this type will be most likely in the case of a highly exothermic reaction. Gaseous oxidation reactions are therefore suitable for investigation.

Hinshelwood and his coworkers have investigated the oxidation of hydrogen, (8, 9, 10, 13), ethylene (14), benzene (3), methane, methyl alcohol, and formaldehyde (4). All these reactions occur by a chain mechanism. Those which involve the oxidation of organic compounds have certain points in common: (1) The reactions possess no simple integral order. The apparent order is high (usually between three and four) and variable. (2) The rate is greatly dependent on the concentration of the organic substance, but is little influenced by the oxygen concentration. (3) Increase in the surface of the containing vessel retards the reactions. (4) The rate of change of pressure accompanying the oxidation attains its full value only after an induction period. Hinshelwood accepts the suggestion of Egerton (2) that the induction periods are due to the initial formation of unstable peroxides which serve as centres from which the chains are propagated.

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It is of interest to accumulate more data concerning such reactions. In addition it is highly desirable to investigate the oxidation of simple organic substances under definite conditions, such as those which prevail in the gaseous state. The present paper deals with the gas-phase oxidation of acetone.

Apparatus

The reaction was investigated by introducing oxygen-acetone mixtures into a heated vessel and observing the rate of change of pressure as the reaction proceeded.

The apparatus employed is illustrated in Fig. 1. The reaction bulb, *A*, of Pyrex glass, was contained in the electric furnace, *B*. The furnace was of a

type which has been previously described (12). Temperatures were measured by means of the chromel-alumel thermocouple, *D*, in conjunction with a Cambridge workshop pattern potentiometer. The temperature was hand regulated by means of a rheostat, and could be kept constant to within 1°C .

The reaction bulb was connected through the Pyrex to soft glass seal, *E*,

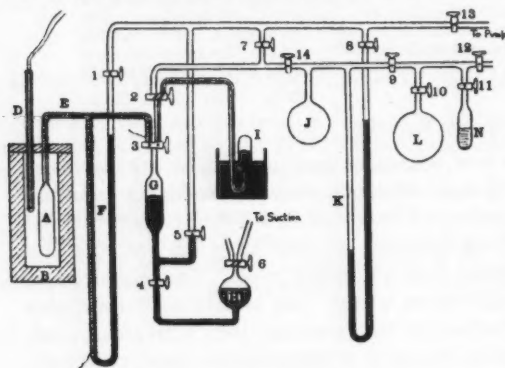


Fig. 1. Diagram of apparatus.

with the capillary manometer, *F*. This manometer and all connecting tubing up to within two or three centimetres of tap 3 was wound with nichrome wire, and maintained at a temperature of 100°C .

Oxygen and acetone were stored in the containers, *L* and *N*. Mixtures of the desired proportions were made up by admitting the gases to the reservoir, *J*, and observing their partial pressures by means of the manometer, *K*.

The oxygen employed was obtained from cylinders, and was purified only by drying over phosphorus pentoxide. It contained about 0.5% of nitrogen.

Acetone was purified by distillation from alkaline permanganate, followed by fractional distillation. It was freed from dissolved air by repeated evacuation.

Experimental Procedure

Prior to making an experiment, suction was applied to bulb *H*, through tap 6. Taps 4 and 5 were opened, and the mercury in the bulb, *G*, and the connecting tubing up to tap 5, was sucked into *H*. Tap 4 was then closed. By suitable adjustment of tap 3, it was then possible to connect the reaction vessel, *A*, to the pumping system for evacuation. The pumping system consisted of a low and a high stage mercury condensation pump in series, backed up by a Hyvac oil pump. Pressures during the process of evacuation were measured by means of a McLeod gauge.

When the system had been thoroughly evacuated, the furnace was brought to the desired temperature as indicated by the thermocouple, *D*. A sample of the oxygen-acetone mixture from the bulb, *J*, was then introduced into the reaction bulb as follows:

Tap 5 was closed and tap 6 was turned so as to connect the bulb, *H*, to the atmosphere. On opening tap 4, mercury entered the bulb *G* from *H*, and was allowed to rise until it had reached some pre-determined level in the bulb *G*, such as the position indicated in the diagram. Tap 7 was then closed, and taps 3, 2, and 14 were turned so as to allow some of the mixture in the reservoir, *J*, to enter the bulb *G*. Tap 3 was then turned to connect *G* with *A*. Tap 4 was opened, and mercury was allowed to follow up the gas, pass through tap 3, and rise about 10 cm. in the capillary above tap 3. In this way the entire space occupied by the reacting gases could be kept hot to prevent the condensation of products, without the necessity of employing a troublesome heated stopcock. The possibility of complications due to the contact of acetone with stopcock grease was also eliminated.

As soon as the reactants had been admitted to *A*, the pressure was read on the capillary manometer, *F*. Pressure readings were then taken at regular intervals of time, and the progress of the reaction was followed by the rate of increase in pressure. The correction for the capillary depression in the manometer, *F*, was made automatically by taking the zero reading of the manometer as the position of the mercury when the system was evacuated. Since relative pressures only are important, no correction was made for the temperature of the mercury in the manometer, and all pressures are expressed in terms of cm. of mercury at 100° C.

The volume of the "dead space" outside the furnace was only about 1% of the volume of the reaction vessel. In consequence it could be neglected without serious error.

In order to withdraw a sample of gas for analysis on the completion of a run, tap 3 was turned so as to connect the reaction vessel to *G*. Tap 4 was opened, suction was applied to *H*, and a sample of the products of reaction was sucked into *G*. Taps 3 and 2 were then adjusted, air pressure was applied to the bulb *H*, and the gaseous sample was forced into the tube, *I*, and collected over mercury.

The Products of the Reaction

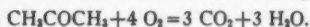
The gaseous products of the reaction were analyzed in a modified type of Bone-Newitt gas analysis apparatus.

The condensable products could be estimated, and the gaseous products referred back to unit quantities of reactants in two ways. First by mixing a known amount of nitrogen or some other inert gas with the original reactants, and calculating back from the amount of nitrogen found in the gaseous products. Secondly by the following method: An inert gas was introduced into the reaction vessel under the conditions which would normally be used in an experiment. The pressure in *A* was noted. A sample was then withdrawn and collected in *I* in the usual manner. The decrease in pressure produced in *A* by the

removal of the sample was noted. The gas in *I* was then transferred completely to the gas analysis apparatus and its volume was measured. In this way the apparatus was calibrated so that the pressure drop which accompanied the removal of a sample indicated its total volume expressed at room temperature and atmospheric pressure. The actual volume of any sample was measured, and the condensable products were determined by difference. Before the measurement, unchanged acetone, or acetic acid, was removed from the sample by absorption with distilled water (15).

The oxidation of acetone in the liquid state, or in solution, has been widely investigated. Very little previous work has been done, however, on the oxidation of gaseous acetone.

White and Price (16) have investigated the explosion limits of acetone-air mixtures, and Holm (11) has measured ignition temperatures. No data are given in these papers concerning the products of the oxidation. Wheeler and Whitaker (15) also investigated oxygen-acetone explosions. They state that on explosion complete oxidation occurs, as indicated by the equation



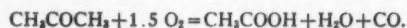
The conditions during explosion are so drastic, however, that this information is of little use in predicting what will occur during the slow oxidation of acetone.

The only direct investigation of the oxidation which the writer has been able to discover is that of Gottlieb (5). He states that the main reaction on passing oxygen-acetone mixtures over a hot surface is the formation of formic and acetic acids,



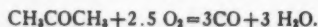
This mechanism receives support from the general chemical behavior of acetone on oxidation under other conditions. The work of Gottlieb is somewhat open to suspicion, however, since it was done in the early days of the development of organic chemistry (1844).

It has been shown by Bone that under the conditions which prevailed in the present investigation formic acid will decompose much more rapidly than it oxidizes (1, pp. 358-400). Hence if Gottlieb's work is correct, we should expect the reaction to be represented by



This would lead to an increase in pressure equal to 50% of the initial concentration of acetone. The actual pressure increase is much higher than this (120 to 150%), the oxygen consumption is greater than that indicated above, and the amounts of carbon monoxide and of condensable products formed are also greater.

It may therefore be concluded that the above reaction is also accompanied by a considerable amount of direct oxidation of acetone to carbon monoxide and water, *viz.*,



A combination of these two modes of oxidation in roughly equal proportions would lead to the pressure increases at completion and to the products found.

A certain amount of carbon dioxide is also found. This may arise by oxidation of carbon monoxide, or, more probably, by a small amount of oxidation of formic acid rather than its decomposition.

It may be pointed out that formaldehyde and methyl alcohol cannot be postulated as products of the oxidation of acetone, since Fort and Hinshelwood (4) have shown that they oxidize at a much faster rate than has been found here for acetone.

For our purpose, however, the important point is not the exact mechanism of the oxidation, but rather to make certain that the pressure increases obtained under different conditions of temperature and concentration are comparable and furnish an indication of the rate at which acetone and oxygen disappear from the system. We will therefore examine the results of the analyses of the products of the reaction at different temperatures, and for different relative proportions of the two reactants.

(A) *The Effect of Temperature on the Products of Reaction*

In Table I are tabulated the average results of a number of analyses of the products formed by the reaction of a mixture containing 1 mole of acetone to 4.05 moles of oxygen at various temperatures. The analyses are given for completion, and also for a pressure increase equal to 50% of the original partial pressure of acetone. These are corrected for the small amount of nitrogen present in the original mixture.

TABLE I
ANALYSIS OF PRODUCTS FROM $1 \text{ CH}_3\text{COCH}_3 + 4.05 \text{ O}_2$

Temperature °C.	Stage	O ₂ %	CO ₂ %	CO %	Condensable (including unchanged acetone), %	CH ₄ %
350	Completion 50%	33.0	6.3	16.1	43.6	1.0
		62.0	1.7	5.1	33.8	0.0
400	Completion 50%	30.0	7.6	18.9	43.4	0.1
		59.9	0.9	7.7	29.5	2.0
450	Completion 50%	32.7	7.5	17.5	42.4	0.0
		60.8	1.6	7.4	28.6	1.6
500	Completion 50%	17.6	9.5	12.5	60.3	0.2
		59.8	1.3	7.6	29.0	2.3

In addition, tests were carried out on the condensable products for acetic acid, and for formaldehyde. Acetic acid was definitely shown to be present in all cases by means of the cacodyl oxide test. No trace of formaldehyde could be detected by means of Schryver's test.

It will be seen from Table I that there is satisfactory correspondence in the analyses at all temperatures at the 50% pressure increase stage. At completion there is also good agreement at 350°, 400°, and 450° C. At 500° C.,

the oxygen consumption is much greater and more condensable products are formed. This is in agreement with the fact that there is a greater total increase in pressure at completion at 500° C., as will be shown later.

It would therefore seem to be justifiable to compare results in the earlier stages of the reaction at all temperatures.

B. The Effect of the Relative Proportions of the Reactants

In Table II are tabulated the analyses of the products of reaction for different mixtures at 450° C. In order to make these comparable they are expressed as per cent of constituents other than oxygen.

TABLE II
ANALYSIS OF PRODUCTS FROM DIFFERENT MIXTURES AT 450° C.

O ₂ /acetone	Stage	CO ₂ %	CO %	Condensable, %	CH ₄ %	CO+CO ₂ , %	CO/CO ₂
4.05	Completion	11.1	26.0	62.9	0.0	37.1	2.3
		4.0	18.8	73.2	4.0	22.8	4.7
2.98	Completion	7.8	28.1	62.7	1.4	35.9	3.6
		4.3	18.6	76.6	0.5	22.9	4.3
2.16	Completion	2.6	35.5	60.1	1.8	38.1	13.7
		4.1	20.7	73.2	2.0	24.8	5.0

The results in Table II show that there is again excellent correspondence in analyses at the 50% stage. At completion there is also fair correspondence, except that, as might be expected, the CO/CO₂ ratio increases as the amount of oxygen in the mixture decreases.

The Pressure Change Accompanying the Reaction

As pointed out above, oxidation to acetic acid and the decomposition products of formic acid would result in a pressure increase equal to 50% of the initial partial pressure of the acetone. Direct oxidation to carbon monoxide and water, on the other hand, would lead to a pressure increase equal to 250% of the initial acetone pressure. The pressure increases actually obtained are given in Table III. These support the conclusion that the actual reaction is a combination of the two possibilities mentioned above. The "final" pressure increases listed were taken when the pressure had remained constant for from 4 to 12 hr. On very long standing (2 to 10 days), especially at the higher temperatures, small erratic pressure changes occurred depending presumably on the slow secondary oxidation of some of the products.

The pressure increase is therefore in the neighborhood of 125%, becoming somewhat higher at high temperatures. This is in accordance with the analytical results, since the products of the reaction change their character somewhat at higher temperatures.

TABLE III
PRESSURE INCREASES AT COMPLETION

Partial acetone pressure, cm.	O ₂ /acetone	Increase in pressure, as % of initial partial pressure of acetone	Partial acetone pressure, cm.	O ₂ /acetone	Increase in pressure, as % of initial partial pressure of acetone
Temperature, 350° C.			Temperature, 400° C.		
4.0	4.95	117.8	9.7	3.10	125.0
7.45	4.95	127.6	9.6	3.65	120.5
7.5	3.03	120.4	3.5	4.35	123.2
9.7	3.03	121.2	7.3	5.00	123.0
16.0	2.00	117.0	8.7	3.00*	123.8
			5.0	3.00†	113.6
Temperature, 450° C.			Temperature, 500° C.		
14.2	2.98	128.0	11.9	2.16	142.6
8.2	4.60	138.6	7.65	2.16	145.9
10.8	4.05	141.1	2.65	2.16	151.0
12.8	2.16	127.5			
13.5	2.16	135.0			

*Plus N₂. †Plus tubing in reaction vessel.

The Velocity of the Reaction

From the previous sections it may be concluded that the rate of pressure change furnishes a sufficiently accurate indication of the rate at which acetone is oxidized. We will therefore consider the velocity of the reaction as inferred from pressure-time curves. The effect of individual factors, such as pressure, concentrations, and temperature, will be considered in detail later.

Some typical data are summarized in Table IV.

The effect of the total pressure on the rate of the reaction is illustrated in Fig. 2, in which pressure increase-time curves are given for the same mixture and temperature, but for varying initial pressures.

The Form of the Reaction Velocity Curves

It will be seen from Fig. 2, and Table IV that there is an induction period at the beginning of the reaction. The maximum rate of change is not reached until a certain time has elapsed. On account of the form of the curves it is impossible to obtain a simple mathematical expression for them. Hinshelwood has successfully derived an equation for such a reaction (4), but this is very complicated and contains a

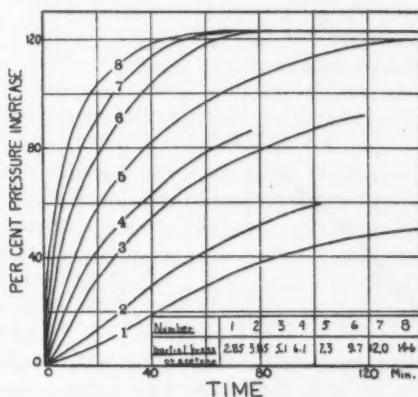


FIG. 2. The effect of pressure on the rate of reaction; 400°C. 1 CH₃COCH₃ + 3.1 O₂.

number of constants which must be evaluated experimentally. The simplest method of ascertaining the effect of various factors on the rate of reaction is therefore to compare the times for some arbitrarily defined fractional change, such as the time to half-value.

TABLE IV
TYPICAL REACTION VELOCITY DATA

Time, min.	Pressure, cm.	Pressure, increase, cm.	Increase, % of initial partial pressure of acetone	Time, min.	Pressure, cm.	Pressure, increase, cm.	Increase, % of initial partial pressure of acetone
400° C. 1 CH ₃ COCH ₃ +5.00 O ₂							
0.0	56.9	0.0	0.0	5	61.65	4.75	51.1
0.5	57.8	0.9	9.7	7	62.65	5.75	61.9
1	58.4	1.5	16.2	11	64.05	7.15	77.0
2	59.4	2.5	26.8	15	65.0	8.1	87.0
3	60.3	3.4	36.5	40	67.45	10.55	113.5
4	61.05	4.15	44.6	Completion	68.2	11.3	121.5
400° C. 1 CH ₃ COCH ₃ +2.03 O ₂							
0	24.9	0.0	0.0	32.5	30.3	5.4	65.8
1	25.15	0.25	3.0	41.5	30.9	6.0	73.2
3	25.35	0.45	5.5	52	31.45	6.55	79.9
7	26.35	1.45	17.7	63.5	31.95	7.05	86.0
11	27.4	2.5	30.5	74	32.3	7.4	90.0
15	28.2	3.3	40.2	Completion	34.7	9.8	119.4
21	29.15	4.25	51.8				
500° C. 1 CH ₃ COCH ₃ +2.16 O ₂							
0.0	29.1	0.0	0.0	3	41.1	12.0	130.5
0.25	30.7	1.6	17.4	4	41.35	12.25	133.0
0.5	33.0	3.9	42.4	6	41.8	12.7	138.0
0.75	35.4	6.3	68.5	8	42.0	12.9	140.1
1.0	36.9	7.8	84.7	10	42.05	12.95	140.8
1.5	39.0	9.9	107.5	20	42.45	13.35	145.0
2	40.15	11.05	120.0	1200	42.45	13.35	145.0

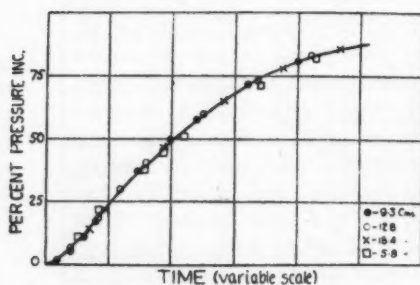


FIG. 3. Affine curves. Varying pressure. 400°C. 1 CH₃COCH₃+2.0 O₂. The pressures given above are the initial partial pressures of acetone.

If such a criterion is used, however, it is necessary to make sure that the form of the curves does not alter appreciably when the various factors affecting the rate are altered. This can be most simply done by determining whether the various curves are "affine". To do this, a set of curves is first plotted in the ordinary way. One curve is then adopted as the standard, and the time scale of the others is altered so as to make one arbitrarily chosen point coincide for all the curves. If the curves

are affine, there will then be complete correspondence throughout their entire length.

Fig. 3 shows curves plotted in this way for a 1:2.0 acetone-oxygen mixture at 450° C., with varying initial pressures. It will be seen that the curves are identical in form throughout their entire length. The relative importance of the induction period is evidently the same for all pressures.

Fig. 4 shows similar curves in which the temperature and the initial acetone pressure are kept constant, while the amount of oxygen varies from 1 to 2, to 1 to 4.6. There is again complete correspondence of the curves at every stage. It would therefore appear that at any particular temperature we are justified in adopting the time for any desired fractional change as a criterion of the rate of the reaction.

The effect of varying temperature on the form of the curve is illustrated in Fig. 5. It is apparent that the strict correspondence of the curves, as shown in Figs. 3 and 4, no longer exists. The form of the curves varies with temperature, the induction period being relatively more pronounced at higher temperatures. The correspondence of the curves at 500°, 450° and 400° C. is good enough in the early stages to allow a sufficiently accurate comparison

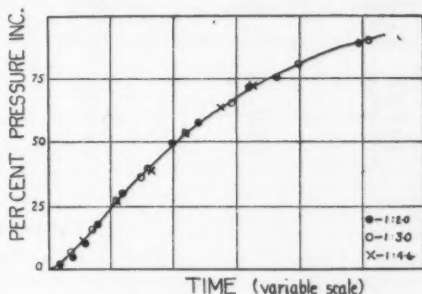


FIG. 4. Affine curves with varying oxygen-acetone ratios. 450° C. Partial acetone pressure, 9.6 cm.

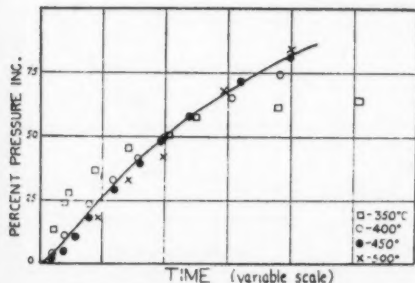


FIG. 5. Affine curves with varying temperatures. Partial acetone pressure, 9.6 cm. $1 \text{ CH}_3\text{COCH}_3 + 2.0 \text{ O}_2$.

sufficiently accurate for all but the curve at 350° C. and merely a rough approximation for this temperature.

The Effect of the Total Pressure on the Rate of the Reaction

The times for the reaction to proceed from 30 to 50% pressure increase under various conditions are given in Tables V, VI, VII and VIII.

TABLE V
VALUES OF $T_{50} - T_{30}$ AT 350° C.

$O_2/\text{acetone} = 2.00$		$O_2/\text{acetone} = 3.03$		$O_2/\text{acetone} = 4.95$	
Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.	Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.	Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.
16.0	5.3	9.7	11	7.4	17
14.9	7.4	7.5	22	7.25	17
11.4	21	5.1	65	4.05	52
9.6	36	4.6	87	1.75	Large
7.5	144	2.3	Large		

TABLE VI
VALUES OF $T_{50} - T_{30}$ AT 400° C.

	$O_2/\text{acetone} = 2.03$								$O_2/\text{acetone} = 3.1$							
Partial acetone pressure, cm.	19.3	14.2	8.2	5.75	14.6	12.0	9.7	7.3	6.1	5.1	3.85	2.85				
$T_{50} - T_{30}$, min.	1.2	2.6	9.1	42.5	1.7	2.5	4.0	7.5	13.5	17	38	71				
	$O_2/\text{acetone} = 3.65$								$O_2/\text{acetone} = 4.35$							
Partial acetone pressure, cm.	13.5	11.3	9.6	7.2	4.9	4.3	3.25	12.5	9.6	7.9	5.6	3.5	2.7			
$T_{50} - T_{30}$, min.	1.7	2.5	3.8	7.0	13.5	22	39	1.4	2.75	4.6	9.8	20	36			
	$O_2/\text{acetone} = 5.00$															
Partial acetone pressure, cm.	9.3			7.3				5.6				5.0				
$T_{50} - T_{30}$, min.	2.7			6.6				9.7				14				

TABLE VII
VALUES OF $T_{50} - T_{30}$ AT 450° C.

$O_2/\text{acetone} = 2.00$		$O_2/\text{acetone} = 2.98$		$O_2/\text{acetone} = 4.60$	
Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.	Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.	Partial acetone pressure, cm.	$T_{50} - T_{30}$, min.
18.4	0.36	16.1	0.24	10.7	0.74
12.8	0.95	14.2	0.47	8.2	0.95
9.3	2.05	9.5	1.20		
5.8	5.8	5.25	3.7		
		4.55	(2.5)		
		4.05	4.4		

TABLE VIII
 VALUES OF $T_{50} - T_{30}$ AT 500° C.

Partial acetone pressure, cm.	$O_2/\text{acetone} = 2.16$				
	11.9	9.2	7.6	4.85	2.65
$T_{50} - T_{30}$, min.	0.19	0.20	0.25	0.64	1.52

Fig. 2 and the foregoing tables show that the rate of the reaction varies rapidly as the pressure varies for all temperatures and relative proportions of the reactants.

The order of the reaction will be given by the relationship

$$T_{50} - T_{30} = \frac{\text{constant}}{P^n - 1},$$

where n is the order and P the initial pressure. For chain reactions the order has no very definite meaning, but it provides a convenient measure of the effect of pressure on the rate of the reaction. From the above relationship it may be seen that $\log (T_{50} - T_{30})$ plotted against $\log P$ should give a straight line, from the slope of which the order may be calculated. A typical

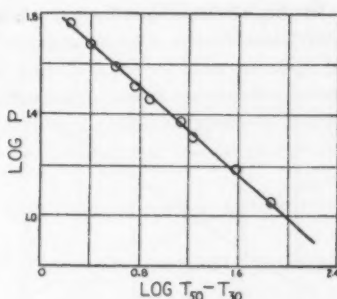


FIG. 6. The logarithm of the total pressure plotted against the logarithm of the time for the reaction to proceed from 30 to 50%. 400° C. $1 \text{ CH}_3\text{COCH}_3 + 3.1 \text{ O}_2$.

curve of this type is given in Fig. 6. From this curve the calculated order is 3.3. In Table IX a summary is given of the orders thus obtained for various mixtures and temperatures.

The order as shown in Table IX is high, not integral, and somewhat variable. This behavior is typical of a reaction which proceeds by a chain mechanism. Other evidence for such a mechanism will be discussed later.

The effect of a variation in the partial pressure of either constituent is shown in Fig. 7. It will be seen that both constituents affect the rate to approximately equal extents. Thus at 400° C. the rate may be approximately expressed by

$$-\frac{d}{dt}(\text{CH}_3\text{COCH}_3) = K (\text{CH}_3\text{COCH}_3)^{1/2} (\text{O}_2)^{1/2}.$$

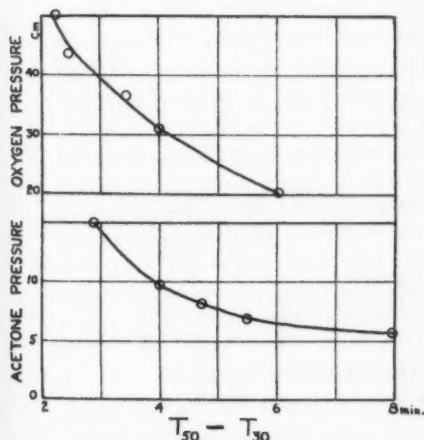


FIG. 7. Influence of separate reactants on the rate of reaction. Upper curve: acetone, 10 cm.; oxygen varying. Lower curve: oxygen, 30 cm.; acetone varying.

TABLE IX
 THE ORDER OF THE REACTION

Temp., °C.	350	350	350	400	400	400	400	400	450	450	500
O ₂ /acetone	2.00	3.03	4.95	2.03	3.10	3.65	4.35	5.00	2.00	2.98	2.16
Order	3.7	3.7	3.2	3.6	3.3	3.2	3.2	3.7	3.2	3.2	2.6

The Temperature Coefficient of the Reaction

In Fig. 8 $\log(T_{50}-T_{30})$ is plotted against the reciprocal of the absolute temperature for a reaction mixture with a partial oxygen pressure of 20 cm., and a partial acetone pressure of 10 cm. The heat of activation calculated from the slope of the line is 26,700 calories per gram molecule. The data from which Fig. 8 was constructed are given in Table X.

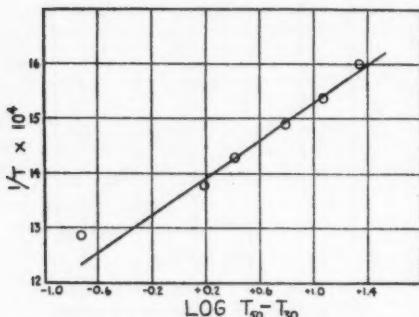


FIG. 8. The temperature coefficient of the reaction.

 TABLE X
 THE TEMPERATURE COEFFICIENT OF THE REACTION

Temperature, °K.	632	648	673	698	723	773
$T_{50}-T_{30}$, min.	21.9	12.0	6.2	2.65	1.58	0.19

Partial oxygen pressure = 20 cm. Partial acetone pressure = 10 cm.

The linearity of the curve in Fig. 8 is only approximate. This is due to the varying relative importance of the induction period, which was mentioned previously (see Fig. 5). Very little weight can be given to the 350° C. point. The heat of activation can therefore be regarded only as an approximate indication of the effect of temperature on the reaction velocity.

The Effect of the Surface of the Reaction Vessel

The effect of surface was investigated by adding tubing to the reaction vessel. About three metres of Pyrex tubing, having an inner diameter of about 3 mm. was added to the vessel in 3-cm. lengths. This would have the effect of shortening the "free path" between the walls of the vessel to at most $\frac{1}{10}$ of its former value, and would increase the total surface about five times. A typical set of results for the packed tube are given in Table XI.

TABLE XI
TIMES FOR THE REACTION TO PROCEED FROM 30 TO 50% IN PACKED TUBE AT 400° C.

	$O_2/\text{acetone} = 3.10$			
	15.5	10.2	9.2	5.0
Partial acetone pressure, cm.				
$T_{50} - T_{30}$, min.	5.1	9.2	9.7	24.5

The pressure-time curves were entirely unaltered in form by the addition of the tubing, as shown in Fig. 9. There is, however, a decided retarding effect caused by the increase in surface. This effect is a well-known characteristic of a chain reaction. The magnitude of the retarding effect may be seen by comparing Table XI with Table VI. The retarding is much more pronounced at high pressures than at low. Thus at a partial acetone pressure of 5 cm., $T_{50} - T_{30}$ is about 1.4 times that for the unpacked tube: at 15.5 cm. it is about 3.2 times greater. This is to be expected, since in the absence of packing the wall factor would be much more pronounced at low pressures than at high. The change in retarding effect with pressure is well shown by calculating the order of the reaction in the packed tube. The order found is about 2.4, as compared with 3.3 for the unpacked tube. In other words, part of the effect of increased pressure on the rate is offset by the increased predominance of the wall factor.

The magnitude of the retarding effect is small compared with that existing in many chain reactions. The indications, therefore, are that under normal conditions most of the chains are broken in the gas, the deactivating influence of the walls being comparatively small, and that the chains, therefore, are not of very great length.

The Effect of Added Nitrogen

Two experiments were carried out in the presence of added nitrogen. The results are shown in Table XII.

TABLE XII
THE EFFECT OF ADDED NITROGEN ON THE RATE OF THE REACTION

	$1 \text{ CH}_3\text{COCH}_3 + 3.10 \text{ O}_2 + 3.05 \text{ N}_2$ 400° C.	
	12.0	7.2
Partial acetone pressure, cm.		
$T_{50} - T_{30}$	1.5	8.3
$T_{50} - T_{30}$ for a similar mixture without nitrogen	1.7	8.0

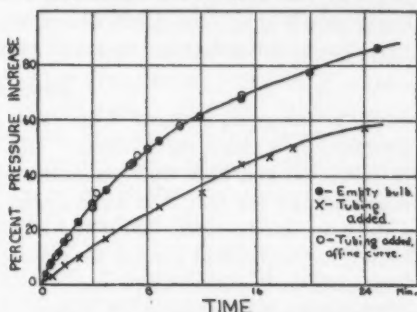


FIG. 9. Affine curves with and without added tubing. 400°C. Partial acetone pressure, 10.2 cm. $1 \text{ CH}_3\text{COCH}_3 + 3.0 \text{ O}_2$.

Nitrogen, therefore, has no appreciable effect on the rate. This points to the same conclusion as in the previous section, *i.e.*, that the chains are comparatively short, and are broken mainly in the gas. If the wall factor were at all pronounced, nitrogen would be expected to increase the rate by keeping the chains off the walls. In the absence of any deactivation at the wall, nitrogen would be expected to have a small retarding effect due to its action as a diluent. The two effects are presumably about equally balanced.

Explosion Limits

A few experiments were made to determine if any concentrations existed at which there was a sharp transition from a slow change to an explosion. Such explosion limits have been shown by Hinshelwood and Thompson to occur with hydrogen-oxygen mixtures. No evidence was obtained for such limits in the oxidation of acetone. At high temperatures explosions occurred if the pressure were sufficiently high, but in all cases the reaction velocity increased continuously up to the point where explosion occurred. The explosions were therefore of the ordinary "thermal" type.

Discussion

In the foregoing sections it has been assumed that the oxidation of acetone proceeds by a chain mechanism. This assumption is supported by a number of facts: (i) the high and variable order, which is a characteristic of such reaction; (ii) the fact that an increase in the surface of the container causes a decrease in the rate; (iii) if the reaction had a real order as high as that found, *i.e.*, somewhat greater than three, it could not possess as high a heat of activation as 26,700 calories and yet proceed at a measurable rate.

The effect of nitrogen on the rate of reaction affords no evidence either for or against the existence of chains. If the reaction involves chains, a foreign gas would be expected to have a marked accelerating effect if the chains were normally broken at the wall. As previously pointed out, the absence of such an effect points to short chains which are mainly broken in the gas.

The temperature coefficient of the reaction throws some light on the mechanism of the process. The heat of activation found is 26,700 calories per gram molecule. A bimolecular reaction proceeding at the same rate would have a heat of activation in the neighborhood of 40,000 calories. In other words, the reaction proceeds more slowly than a bimolecular reaction with the same heat of activation. It would naturally be expected that a chain reaction would be faster than the corresponding bimolecular reaction.

It should be remembered, however, that there are indications that the reaction changes its course somewhat with changing temperature. In consequence, too much reliance must not be placed on any conclusions drawn from considerations of the heat of activation. The fact that the observed heat of activation is low may therefore be due to this cause, although it is doubtful if the change in the course of the reaction is sufficiently great to account for the discrepancy.

The low heat of activation might also be explained on the assumption that the process initiating the chains is termolecular rather than bimolecular. If

this were the case it would be necessary to postulate chains having a length of 10^3 to 10^4 molecules in order to explain the observed rate. This is out of the question in view of the evidence previously considered for short chains.

There is, however, no reason why the chain length should remain constant as the temperature is varied. If the chain length varies with temperature, the observed heat of activation will be a composite one, and will include the temperature coefficients of the initial process, and of the variation in chain length. Under these conditions no correlation will be possible between the heat of activation of the reaction, and that of a simple reaction.

The most probable explanation, therefore, would seem to be that the chains are short, that their length varies with temperature, and that the process initiating the chains is bimolecular.

The existence of an induction period must mean that products are accumulating in a manner which does not involve an increase in pressure. Egerton (2) suggests that the first stage in the oxidation of a hydrocarbon is the formation of an unstable peroxide, which provides the centre from which reaction chains commence. Fort and Hinshelwood (4) have given strong evidence that this is true of the oxidation of organic substances in general. Hatcher, Miss Howland, and the author (6, 7) have proved definitely that such a peroxide accumulates in the initial stages of the oxidation of gaseous acetaldehyde. It is therefore reasonable to assume that the induction period in the oxidation of acetone is due to the initial formation of a peroxide in the same way.

The oxidation of acetone differs from most oxidation reactions of the chain type in one important respect. The two reactants are of about equal importance in so far as the effect of their concentrations on the rate are concerned. They would therefore appear to be equally efficient in the propagation of chains.

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STUDIES OF POLYMERS AND POLYMERIZATION

V. THE INFLUENCE OF METHYL AND PHENYL SUBSTITUTION ON THE POLYMERIZABILITY OF BUTADIENE¹BY GEORGE STAFFORD WHITBY² AND WILFRED GALLAY³

Abstract

A number of methyl- and phenyl- substituted butadienes were prepared and polymerized by different means under properly comparable conditions. The velocity and extent of polymerization were measured and the influence of the number and position of substituent groups on these two factors are discussed. The extent of polymerization depends upon the number of unsubstituted hydrogen atoms on the terminal carbon atoms of the conjugated system, and the ability of a conjugated diene to form a synthetic rubber depends upon the presence of at least three of these hydrogen atoms. The presence of phenyl substituents favors a tendency to dimer formation. The dimers from all the hydrocarbons were unsaturated ring compounds. 1-Phenyl-3-methyl butadiene and 1-3-diphenyl butadiene were found to polymerize spontaneously. The action of methyl magnesium iodide on benzalacetophenone results in both 1-2 addition to yield 1-3 diphenyl buten-1-ol-3, and in 1-4 addition to yield 2-4-diphenyl butanone-4, the former reaction preponderating.

In the last paper of the present series (26) a comparison of the polymerization of isoprene and 2-3-dimethylbutadiene-1-3 was recorded. In the present study a larger number of substituted butadienoid hydrocarbons, *viz.*, nine methyl-substituted and four phenyl-substituted hydrocarbons, has been examined, with the object of ascertaining the influence of the amount and kind of substitution on the ease and degree of polymerization.

The results make it clear that the presence of an unsubstituted terminal methylene group in these hydrocarbons is favorable to the occurrence of polymerization. They also indicate that in general increase in the number of substituent groups of a given kind reduces the ease of polymerization, especially to high molecular products.

Table I shows the results obtained in a comparison of the polymerization of all the five isomeric dimethylbutadienes under identical conditions.

The isomers fall in the same order as regards speed of polymerization in the experiments at both the temperatures employed. The isomer (2-3) in which there is no terminal substitution polymerizes most quickly and that (1-4) in which there is substitution at both ends of the butadienoid system least quickly. The *gem*-dimethyl compound (1-1) underwent polymerization to a greater extent but to a lower degree than the 1-4 compound, the "higher polymer" from it being only an oil of relatively low molecular weight. The "higher polymer" from the 2-3 and from the 1-3 compounds was an elastic, rubber-like solid. The 1-2 compound gave in the present experiments a firm gel which could perhaps hardly be described as rubber-like. A soft, rubbery polymer has however been obtained from this diene by Fisher (6).

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TABLE I
 POLYMERIZATION OF THE DIMETHYLBUTADIENES-1-3 BY HEAT

	Hydrocarbon (Position of methyl groups)				
	2-3	1-2	1-1*	1-3	1-4
A. 30 Days at 100° C.					
Increase in d_4^{20}	—	0.0630	0.0669	0.0469	0.0197
Increase in d_D^{20} , %	—	8.5	9.5	6.5	2.8
Increase in n_D^{20}	0.0561	0.0185	0.0158	0.0084	0.0061
Increase in n_D^{20} , %	3.90	1.21	1.09	0.59	0.42
Total polymerization, %	100	91	57	51	33
Dimer formed, %	54	53	43	32	20
Higher polymers, %	46	38	14	19	32
Mol. wt. of higher polymer	1377	919	432	1334	795
B. 15 Days at 150° C.					
Increase in d_4^{20}	0.1360	0.1172	0.0972	0.0968	0.0789
Increase in d_D^{20} , %	17.2	15.7	13.6	13.3	10.9
Increase in n_D^{20}	0.0439	0.0327	0.0267	0.0215	0.0171
Increase in n_D^{20} , %	3.05	2.25	1.85	1.49	1.17
Total polymerization, %	100	100	83	78	68
Dimer formed, %	63	73	59	59	51
Higher polymers, %	37	27	24	19	17
Mol. wt. of higher polymers	1184	674	304	1002	602

*See remarks in the experimental part concerning the chemical identity of this preparation.

It may be noted that Lebedev (15) found the terminally substituted piperylene (1-methylbutadiene) to polymerize less readily than isoprene (2-methylbutadiene). On heating at 150° C. for 15 hr. he found these hydrocarbons to undergo polymerization to the extents of 30% and 79% respectively.

The polymerization of all five dimethylbutadienes at both 100° C. and 150° C. leads to the formation of a large amount of oily dimer. The proportion of dimer to higher polymer formed is greater at the higher than at the lower temperature (cf. 26). The 1-1 and 1-2-dimethylbutadienes yielded two dimers. In the case of each of the other three dimethylbutadienes the evidence indicated that only one dimer was formed. Determinations of the degree of unsaturation indicated that all the dimers were ring compounds and hence incapable of further polymerization. The dimers of 2-3-dimethylbutadiene have previously been examined by Whitby and Crozier (26) and those of isoprene have been

examined with great care by Whitby and Crozier (26) and by Wagner-Jauregg (24). They were found to consist of ring compounds, open-chain dimers being absent.

Experiments on the polymerization of two trimethylbutadienes, namely, the 1-1-3 and 1-1-4 compounds showed (a) that terminal substitution retards polymerization, since the latter compound showed a smaller tendency to polymerize than the former, (b) that the additional substitution, as compared with that in the dimethylbutadienes, retards polymerization. While sulphuric acid polymerized 1-1-3-trimethylbutadiene to the extent of 81%, yielding polymeric material as high in part as a pentamer, it was without action on 1-1-4-trimethylbutadiene under the same conditions. When polymerized by means of heat, the two isomers gave the results shown in Table II.

TABLE II
POLYMERIZATION OF TRIMETHYLBUTADIENES

Heat treatment	Total polymerization, %	Dimer, %	Higher polymer, %	Mol. wt. higher polymer
A. 1-1-3-Trimethylbutadiene				
13.5 days at 85° C.	10	1	9	—
28 days at 85° C.	14	1	13	348
30 days at 85° C. and } 38 days at 140° C.	63	35	28	374
B. 1-1-4-Trimethylbutadiene				
13.5 days at 85° C.	Trace	0	Trace	
38 days at 140° C.	24	20	4	

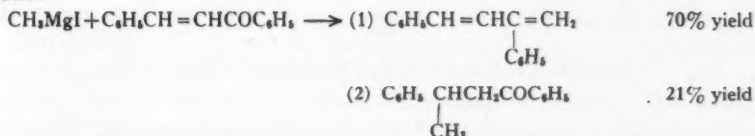
It will be noted that the 1-1-3 compound polymerizes less than either the 1-1 or 1-3 dimethyl compounds, and similarly that the 1-1-4 compound polymerizes less than the 1-1 or 1-4 dimethyl compounds.

Experiments with two tetramethylbutadienes also show that terminal substitution retards polymerization, and, when the results are compared with those for the di- and tri-methyl compounds, that increase in the degree of substitution is unfavorable to polymerization. The 1-1-4-4 compound, in which all the terminal hydrogens of the butadiene chain are substituted, was considered by Pribytek (19) to show inclination to polymerize and has been mentioned in the patent literature as polymerizable (4), but Lebedev (15) found it to yield only a trace of polymer when heated for 90 days at 150° C. On the other hand, 1-2-3-4-tetramethylbutadiene, which was first prepared by Macallum and Whitby (17) and found to undergo very little change in four days at 100° C., has, in the present experiments, been found to polymerize to the extent of 80% in five days at 235° C., nearly half the polymeric product having a molecular weight corresponding to a pentamer.

Just as 1-phenyl butadiene polymerizes much faster than butadiene, so

1-phenyl-3-methyl butadiene (phenyl isoprene) has been found to polymerize much more quickly than isoprene. In fact no unpolymerized hydrocarbon could be isolated from the preparation. Grignard (7, p. 486) and Klages (11) also have noted that this hydrocarbon polymerizes quickly on heating. The dimer produced possesses a ring structure and was found incapable of undergoing further polymerization. Results given in the literature indicate that although phenyl-substituted butadienes polymerize more readily than corresponding methyl-substituted compounds, they polymerize generally to ring dimers only; in no case have they yielded high, rubber-like polymers.

2-3-Diphenyl butadiene has been reported to polymerize rapidly at room temperature (10, 22). 1-3-Diphenyl butadiene (hitherto unknown) showed such remarkable tendency to undergo polymerization that the latter reaction took place partially in cold ethereal solution, the insoluble dimer being precipitated. No unpolymerized hydrocarbon was recovered and no polymer other than the dimer was isolated. Attempts to polymerize this dimer further by various means were unsuccessful. The action of methyl magnesium iodide on benzalacetophenone resulted in both 1-2 addition to yield the corresponding tertiary alcohol and in 1-4 addition to yield the corresponding saturated ketone.

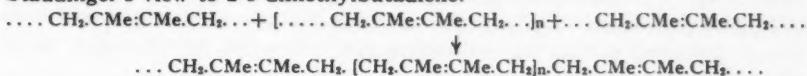


In contrast to the 2-3 and 1-3 compounds, 1-4 diphenyl butadiene, with its two terminal substituents, was found to be stable at temperatures below the melting point (150° C.) and only above that temperature did polymerization take place. By heating for five days at 235° C., there was obtained a gelatinous polymer of low degree of polymerization and by treatment with antimony pentachloride was obtained an amorphous gray powder, mol. wt. 962.

The isomeric 1-2-3-4 and 1-1-4-4 tetraphenyl butadienes were found to be but little affected by heating for five days at 235° C. By the action of antimony pentachloride, the 1-1-4-4 compound, in which all the terminal hydrogens of butadiene are substituted, remained practically unchanged whereas the 1-2-3-4 compound yielded a polymer of mol. wt. 1090.

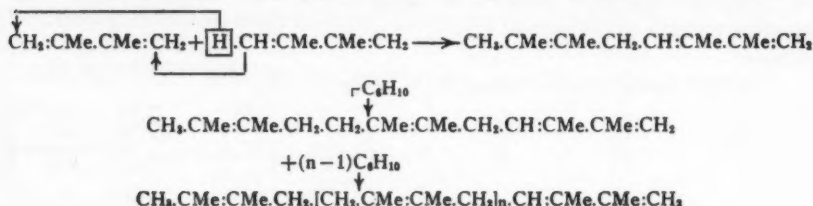
Although the present study does not afford any conclusive evidence as to the mechanism of the polymerization of methyl-substituted butadienes to high polymers and as to the structure of the latter, it is not without a bearing on this question.

Staudinger considers the polymerization of isoprene to caoutchouc to involve the mutual, partial 1-4 addition of isoprene molecules to form long chains with free terminal valencies (21). The following scheme shows the application of Staudinger's view to 2-3-dimethylbutadiene.



According to this scheme of polymerization, no wandering of hydrogen atoms takes place. On the other hand, the scheme of polymerization of isoprene to caoutchouc which has been advanced by Whitby (25), as an outcome of earlier studies in this series (27, 28), involves as an essential feature the wandering of hydrogen. According to this scheme the polymerization of conjugated dienes to high polymers involves the addition of successive molecules with wandering of a terminal hydrogen atom at each step. In view of the fact that the present study shows the importance of free terminal hydrogen atoms in the polymerization of substituted butadienes in favoring polymerization, it may be said that the results of this study accord well with such a scheme of polymerization. Complete terminal substitution, as in 1-1-4-4-tetramethyl and -tetraphenyl butadienes, prevents polymerization altogether; partial substitution of the terminal hydrogens retards it, possibly through steric hindrance.

Applied to 2-3-dimethylbutadiene, the scheme of Whitby may be shown as follows. Since the main product of ozonolysis is acetonyl-acetone (8, 9) it is clear that the addition takes place in the 1-4, not the 1-2, sense.



Experimental

Dimethylbutadienes

2-3-Dimethylbutadiene. This was prepared by the dehydration of pinacol by means of hydrobromic acid. B.p., 69-70° C.; n_D^{20} , 1.4375; d_4^{20} , 0.7263; yield, 80%.

1-3-Dimethylbutadiene. The tertiary alcohol, 4-methyl penten-2-ol-4, prepared from ethylidene acetone and methyl magnesium iodide, was dehydrated by means of hydrobromic acid (13). B.p., 76-77° C.; n_D^{20} , 1.4418; d_4^{20} , 0.7215.

1-2-Dimethylbutadiene. Tiglic aldehyde (16) was prepared by heating freshly prepared acetaldehyde and propionaldehyde in aqueous sodium acetate solution for 28 hr. at 100° C. in an autoclave fitted with a stirrer. After rising to 95 lb. per sq. in., the pressure slowly dropped to below atmospheric. The aldehyde layer was separated and the by-products, consisting mainly of crotonaldehyde and methylethylacrolein, removed by fractionation in an atmosphere of carbon dioxide. Yield, 40% based on the propionaldehyde; b.p., 114-117° C. By treatment of the tiglic aldehyde with methyl magnesium iodide, the secondary alcohol, 3-methyl penten-2-ol-4, was obtained (1). B.p., 88-90° C./115 mm.; yield, 75%. The alcohol was dehydrated to the desired hydrocarbon by means of hydrobromic acid. Dehydration of the secondary alcohol occurred with greater difficulty than in the succeeding case. B.p., 76-79° C.; n_D^{20} , 1.4528; d_4^{20} , 0.7452.

1-4-Dimethylbutadiene. The secondary alcohol, hexen-2-ol-4, was prepared from carefully purified crotonaldehyde and methyl magnesium iodide (20). B.p., 85-87° C./118 mm.; yield, 85%. Dehydration by hydrobromic acid gave the desired hydrocarbon in 65% yield. (Potassium bisulphate gave only a 10% yield.) B.p., 80-82° C.; n_D^{20} , 1.4502; d_4^{20} , 0.7167.

1-1-Dimethylbutadiene. Diacetone alcohol was reduced to 2-methyl pentandiol-2-4 by means of sodium amalgam (29). The crude diol (65% yield) was purified by fractionation at 1 mm. (50% yield). It was dehydrated by means of hydrobromic acid (14), after potassium acid sulphate had been found to give very poor yields. The diol (100 cc.) was heated for three hours under a Hempel column with 2 cc. 48% HBr and pumice, the heating being controlled so as to keep the vapor temperature below 95° C. A further 100 cc. of the diol was then added and heating continued, a little more HBr being added during the latter part of the operation to replace loss. The resultant clear liquid was separated from the aqueous layer, dried over potassium carbonate and fractionally distilled. The product was dried over calcium chloride and again fractionated. B.p., 76-77° C.; n_D^{20} , 1.4472; d_4^{20} , 0.7204; yield in the dehydration, 30%.

Since this work was done an examination of the hydrocarbon obtained by the dehydration of the glycol in question has been carried out by Diels and Alder (3, pp. 68-73, 98-101) and by Farmer, Lawrence and Scott (5), who conclude that the product is 1-3-, not 1-1-, dimethylbutadiene. The product obtained by the present authors, however, differs from the 1-3 isomer noticeably in density and refractive index (*vide supra*) and, above all, in its behavior on polymerization. In polymerization experiments with the authors' preparations there is a noticeable difference in the speed of polymerization (see Table I) and in the nature of the dimeric oily products, and there is a very great difference in the character of the higher polymer formed, that from the 1-3 isomer being rubber-like, while that from the 1-1 isomer was an oil. It must be considered probable that while, as Diels and Alder's investigations indicate, the hydrocarbon product obtained by the dehydration of the glycol prepared by the reduction of acetone alcohol, contains some 1-3-dimethylbutadiene, yet, as employed in the present study, it was preponderantly the 1-1 compound.

Polymerization by heat. Each hydrocarbon (10 gm.), freshly distilled, was heated in sealed tubes of approximately the same capacity, for 15 days at 150° C. and for 30 days at 100° C. The density and refractive index after heating were measured in each case. The contents of each tube was distilled, unchanged monomer being first removed at atmospheric pressure, and dimeric products then separated under reduced pressure. In no case could any product higher than a dimer be distilled off without decomposition. The higher polymeric material remaining after the distillation was purified by precipitation with alcohol from solution in benzene. After two repetitions of this purification process and drying *in vacuo*, the molecular weight of the higher polymer was determined cryoscopically in benzene at the same concentration in all cases.

The main results of these comparative polymerization experiments have been given in Table I. The results of an examination of the dimeric products are recorded below.

Inspection of the tubes during the periods of heating indicated the differences in the rates of polymerization of the isomers which the data in Table I reveal in quantitative terms. At 150° C., after three days the 2-3 compound had changed to a very viscous oil; after seven days this compound had become a barely fluid, glass-like mass, while the 1-2 compound appeared more viscous than originally and the other compounds had not noticeably increased in viscosity. At 100° C., after 15 days the compounds were similar in appearance to what they were after seven days at 150° C.

The higher polymeric material isolated at the end of the heating periods had the following character. From the 2-3 and 1-3 compounds it was a white, elastic solid, more readily soluble in benzene in the latter than in the former case. From 1-2-dimethylbutadiene the higher polymer obtained at 100° C. was a rather oily, firm gel, while that obtained at 150° C. was a gelatinous sticky solid. It is not improbable that at a lower temperature than 100° C., the 1-2 isomer would yield a rubber-like product. Indeed Fisher (6) has reported that he obtained a soft rubbery product from this diene by heating at 100° C. with benzoyl peroxide or in the presence of air. From the 1-4 compound the product at 100° C. was a softer gel than from the 1-2 compound; and at 150° C., a viscous oil. The 1:1 compound gave only an oil. The latter was not purified for the molecular weight determination, as it could not be reprecipitated from solution.

Dimers. Dimers isolated after the heat polymerization of the dimethylbutadienes were as follows.—

(1) 2-3-Dimethylbutadiene gave only one dimer. B.p., 95° C./17 mm.; n_D^{20} , 1.4815; mol. wt., 167 (calc., 164). Iodine absorption per mol., 1.82 mol.

(2) 1-2-Dimethylbutadiene gave two dimers, the second in very small amount only.

(a) B.p., 97-100° C./16 mm.; n_D^{20} , 1.4815; mol. wt., 165 (calc., 164). Iodine absorption: 1.73 mol. per mol.

(b) B.p., 108-110° C./16 mm.; n_D^{20} , 1.4850.

(3) 1-1-Dimethylbutadiene gave two dimers, the higher boiling one in very small amount:

(a) B.p., 94-97° C./16 mm.; n_D^{20} , 1.4752; mol. wt., 164. Iodine absorption: 1.71 mol. per mol.

(b) B.p. 105-108° C./16 mm.; n_D^{20} , 1.4800.

(4) 1-3-Dimethylbutadiene gave only one dimer. B.p. 90-92° C./16 mm.; n_D^{20} , 1.4758; mol. wt., 167. Iodine absorption: 1.94 mol. per mol.

(5) 1-4-Dimethylbutadiene gave two dimers, the higher boiling one in very small amount.

(a) B.p. 90° C./20 mm.; n_D^{20} , 1.4695; mol. wt., 166. Iodine absorption: 1.90 mol. per mol.

(b) B.p. 96-98° C./20 mm.

The iodine absorption was determined by means of Hanus solution applied in 50% excess for 24 hr. The results, although consistent, were somewhat low, possibly due to the time allowed for absorption being insufficient. Concordant results could not be obtained with a solution of bromine in chloroform, although this reagent was used successfully with other dimers (*infra*).

Polymerization by catalysts. To 5 cc. of each of the dimethylbutadienes was added 3 cc. of a 20% solution of stannic chloride in chloroform. Much heat was evolved and highly colored solutions were obtained. After four hours' standing, the solutions were diluted with 10 cc. of chloroform and were poured into a large excess of absolute alcohol. Only from 2-3-dimethylbutadiene was a solid polymeric product obtained; from the other isomers the precipitate consisted of a small amount of a reddish oil containing halogen and of about the same specific gravity as the chloroform-alcohol mixture.

1-1-3 and 1-1-4 Trimethyl butadienes. 2-4-Dimethyl penten-2-ol-4, prepared by the action of methyl magnesium iodide on mesityl oxide, was dehydrated to 1-1-3-trimethyl butadiene-1-3 by distillation under atmospheric pressure*. B.p., 92° C./749 mm. Grignard (7, p. 478) gives the boiling point as 92-93° C./750 mm. Yield, 50% based on mesityl oxide used.

5-Methyl hexen-2-ol-4 was prepared by the action of isopropyl magnesium bromide on crotonaldehyde (20). The yield of redistilled alcohol (B.p. 90-93° C./100 mm.) was 60% based on the crotonaldehyde used. By the use of 48% hydrobromic acid dehydration to 1-1-4-trimethyl butadiene-1-3 was effected in 55% yield as compared with 10% yield using KHSO_4 . B.p., 97-99° C.; n_D^{20} , 1.4585; d_4^{20} , 0.7461.

Polymerization of the trimethyl butadienes by sulphuric acid. The same procedure was used for each of the hydrocarbons. The hydrocarbon (10 gm.) was added dropwise with stirring to 90 gm. of 80% sulphuric acid cooled in ice. After standing at 0° C. for $\frac{1}{2}$ hr., with frequent shaking, the reaction mixture was poured on chipped ice and the whole extracted three times with ether. The ethereal solution was washed with sodium bicarbonate and then with water. It was dried over anhydrous sodium sulphate and the ether removed.

In the case of the 1-1-4 isomer, the remaining liquid was distilled under atmospheric pressure and the original hydrocarbon obtained in almost 100% recovery.

In the case of the 1-1-3 isomer, 9.1 gm. of a viscous, colorless oil remained which was fractionally distilled. After removal of the monomer, distillation under reduced pressure yielded two fractions besides a small amount of a non-distillable residue. Total polymerization, 81%: 1st fraction, 60; 2nd fraction, 11; Residue, 10.

Fraction I—B.p. 87-89° C./8 mm., n_D^{20} , 1.4804, mol. wt. 185 (calc. for dimer, 192). Unsaturation determination (Hanus method) showed 1.86 mol. iodine absorbed per mol. of hydrocarbon. A dimer prepared by the action of 80% sulphuric acid on the diene is described by Grignard (7, p. 478): b.p., 98-100°

* For this preparation the authors are indebted to R. N. Crozier.

C./12 mm.; n_D^{10} , 1.48483. Fraction II—B.p. 170-175° C./4 mm., mol. wt. 282 (calc. for trimer 288); C, 86.8; H, 12.2% (calc. for polymer: C, 87.5; H, 12.5%). Mols. iodine absorbed per mol. of hydrocarbon, 1.80 (Hanus method). Residue—Mol. wt. 471 (calc. for pentamer 480).

Polymerization of the trimethyl butadienes by heat. (a) Three samples of 1-1-3-trimethylbutadiene were heated under conditions listed and then remained sealed at room temperature for about one year before examination. Fractional distillation yielded the following results which have been recorded in Table II. The dimer has been described above. The higher polymer from Sample No. 1 was a viscous, gelatinous oil, mol. wt. 374 (calc. for tetramer, 384); C, 87.8; H, 12.2% (calc. 87.5, 12.5%). Mol. wt. of the higher polymer from Sample No. 2 was 348.

(b) Two samples of 1-1-4 trimethylbutadiene were heated under conditions listed and then fractionally distilled. Results have been given in Table II. The dimer was a colorless liquid; B.p., 92-95° C./8 mm.; n_D^{20} , 1.5037; mol. wt., 198 (calc. 192). Absorption of iodine: 1.90 mol. per mol.

(c) By the action of stannic chloride and antimony pentachloride on 1-1-4 trimethylbutadiene as described in the case of the dimethyl butadienes, there were obtained only small amounts of reddish oils containing halogen and of about the same specific gravity as the chloroform-alcohol mixture.

1-2-3-4 Tetramethylbutadiene-1-3. Methyl ethyl ketone was reduced to 3-4 dimethyl hexandiol-3-4 by amalgamated magnesium in benzene solution (17). B.p. 124-127° C./55 mm.; yield, 30%. By means of a trace of dilute sulphuric acid the diol was dehydrated to the desired hydrocarbon. B.P., 71-73° C./100 mm.; yield, 75%.

A sample of the hydrocarbon was heated in a sealed tube for five days at 235° C. and then fractionally distilled. The total polymerization was 80%, of which 45% was Fraction 1, 20% Fraction 2 and 15% undistillable residue. Fraction 1—B.p., 127-123° C./14 mm.; n_D^{20} , 1.4900; mol. wt., 229 (calc. for dimer 220); iodine absorption, 2.14 mol. per mol. of hydrocarbon. Fraction 2—B.p., 170-180° C./10 mm.; mol. wt., 304 (calc. for trimer 330); iodine absorption, 1.74 mol. per mol. Residue—Mol. wt., 504 (calc. for pentamer 550). On treatment with stannic chloride and antimony pentachloride the diene gave only small amounts of colored oils containing halogen.

1-3-Diphenyl butadiene-1-3. The method attempted for the preparation of the hydrocarbon was the interaction of methyl magnesium iodide and benzyldiene acetophenone to yield the corresponding tertiary alcohol with subsequent dehydration of the latter. The product proved to be a dimer of the desired hydrocarbon.

Benzalacetophenone was prepared by the condensation of benzaldehyde and acetophenone in alkaline solution. The ethereal solution of the benzalacetophenone was added very slowly to the methyl magnesium iodide, with strong stirring to avoid local heating, and the temperature of the reacting mixture was kept at -10° C. After hydrolysis of the complex, the ethereal solution was washed successively with 5% sodium hydroxide, sodium bisulphite and

water, dried over anhydrous sodium sulphate, and the ether was removed. The resultant liquid was allowed to stand overnight when a considerable mass of light yellow solid containing a small amount of an oil separated out. The precipitate was collected and washed repeatedly with alcohol warmed to about 40° C. The solid was recrystallized from alcohol (the treatment of the filtrate is described in a later section). Yield: 70%. The recrystallized material consisted of very fine, white crystals, m.p. 167° C., soluble in benzene, chloroform and boiling alcohol. C, 93.8; H, 6.9% (calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%); mol. wt., 414 (calc. for a dimer of this hydrocarbon; 412). Two unsaturation determinations, carried out with a bromine solution in chloroform, gave 2.09 and 2.05 mol. bromine absorbed per mol. of hydrocarbon.

Small amounts of this ring dimer were sealed in tubes and heated for varying lengths of time, but in all cases the dimer was recovered practically unchanged. Stannic chloride and antimony pentachloride had no action on a chloroform solution of the dimer beyond developing a slight greenish color.

It was expected that the filtrate after separation of the dimer would contain essentially the desired alcohol, 1-3-diphenyl buten-1-ol-3. Accordingly the oil was refluxed with an excess of acetic anhydride for 2 hr. No precipitate appeared on cooling. The oil was taken up in ether, washed with dilute sodium hydroxide, then with water, and dried over anhydrous sodium sulphate. The ether was removed, and the oil allowed to stand for several days in the cold, when crystallization took place. Yield: 21%. The crystals were soluble in all organic solvents. They were finally recrystallized from 50% methyl alcohol with much loss. The product appeared to be 1-3-diphenyl butanone-1. M.p., 74° C.; mol. wt., 224 (calc. for $C_{16}H_{16}O$, 224); C, 85.8; H, 7.3% (calc. for this ketone: C, 85.7; H, 7.1%).

1-Phenyl 3-Methyl butadiene 1-3. Recrystallized benzal acetone in ethereal solution was added dropwise with stirring to a solution of methyl magnesium iodide at -10° C. After hydrolysis of the Grignard complex, the ethereal extract was separated, washed successively with dilute sodium hydroxide solution, sodium bisulphite solution and finally with water. After drying over anhydrous potassium carbonate, the ether was removed, a yellow oil remaining. Without further purification this oil was dehydrated. It was treated with an excess of acetic anhydride and the solution heated over a boiling water bath for three hours. Then the solution was distilled under 150 mm. pressure and the acetic anhydride and acetic acid removed. According to Grignard (7, p. 486), the desired hydrocarbon boils at 115° C./18 mm. (cf. 11). However, in this instance, no distillate was obtained, even after lowering the pressure to 4 mm. and raising the temperature to 160° C. It was concluded, then, that no monomeric hydrocarbon was present and that the resulting viscous brown liquid contained the hydrocarbon in polymerized form. The material was very soluble in benzene and chloroform, and alcohol failed to throw out any product, indicating the absence of any high polymer.

The oil (35 gm.) was then distilled from a Claisen flask in an atmosphere of carbon dioxide. A few drops distilling at 100° C./2 mm. were discarded. A

clear light yellow oil (10 gm.), distilling at 180-185° C./2 mm., was collected. No further distillate could be obtained without decomposition. Mol. wt. 296 (calc. for dimer of 1-phenyl 3-methyl butadiene, 288): C, 92.02; H, 8.00% (calc. for above dimer, C, 91.7; H, 8.3%). In two determinations 1.88 and 1.93 mol. respectively of bromine was absorbed per mol. of hydrocarbon from a solution of bromine in chloroform.

It was attempted to polymerize further this ring dimer by heating small amounts in sealed tubes for 15 days at a temperature of 250° C., with and without sodium. In all cases the dimer remained unchanged. Heating at 100° C. with benzoyl peroxide produced no change. Stannic chloride did not exert any apparent effect, no heat being evolved and no color change apparent.

1-4-Diphenylbutadiene-1-3 (trans-trans). The hydrocarbon was prepared by the condensation of cinnamic aldehyde and phenyl acetic acid according to the procedure of Kuhn and Winterstein (12, p. 103). After recrystallization from acetic acid, there were obtained light yellow large crystals showing green and blue fluorescence, m.p. 150° C.

The hydrocarbon (10 gm.) dissolved in 150 cc. chloroform was treated with 10 cc. of a 20% solution of anhydrous antimony pentachloride in chloroform. The solution became warm and turned violet in color. After three days' standing it was poured into a large excess of absolute alcohol. The precipitate, about 2 gm. of a gray amorphous powder, was purified by reprecipitation twice by absolute alcohol from benzene solution. M.p. 243-250° C.; mol. wt., 962 (calc. for pentamer, 1020). A sample of the hydrocarbon was heated for five days, at 235° C. There was produced a gelatinous viscous oil, readily soluble in benzene.

1-2-3-4 Tetraphenyl butadiene-1-3 and 1-1-4-4-tetraphenyl butadiene-1-3. Desoxy benzoin pinacone, prepared by the reduction of benzoin by zinc dust in acetic acid (2), was dehydrated to the first-mentioned hydrocarbon by means of acetyl chloride (18). The product was recrystallized from glacial acetic acid. M.p., 183° C. Yield on dehydration, 30%.

In order to obtain the second-mentioned hydrocarbon, tetraphenyl tetramethylene glycol was prepared by the action of phenyl magnesium bromide on ethyl succinate in ethereal solution (23). After hydrolysis of the complex and separation of the ether layer, the required glycol precipitated from the latter in the cold on standing. M.p., 206° C.; yield, 70%. Dehydration was effected by boiling in glacial acetic acid solution with a large excess of conc. HCl. M.p., 202° C.; yield on dehydration, 90%.

Polymerization by antimony pentachloride. Each hydrocarbon (10 gm.) was dissolved in 120 cc. of chloroform and 10 cc. of a 20% anhydrous halide solution in chloroform added. In the case of the 1-2-3-4 compound, the reaction mixture became warm and turned deep violet in color. The 1-1-4-4 isomer developed little heat of reaction with only a faint blue color. After standing for three days, the solutions were poured into a large excess of absolute alcohol and the resultant precipitates purified by twice dissolving in chloroform and precipitating with alcohol. The products were then twice extracted with

boiling glacial acetic acid in order to remove unchanged monomer. The product from the 1-1-4-4 isomer was totally soluble in this medium and when recrystallized from it melted at 197° C. (m.p. monomer, 202° C.), mol. wt. 372 (calc. for monomer, 358). In the case of the 1-2-3-4 isomer, a small amount of a reddish-yellow amorphous powder remained after the acetic acid extraction. Heating to 350° C. left the solid unmelted. Mol. wt. 1090 (calc. for trimer 1074).

Polymerization by heat. A sample of each hydrocarbon was heated in a sealed tube at 235° C. for five days. The products were dissolved in benzene and precipitated with alcohol. The product from the 1-2-3-4 diene was a sticky, glass-clear, viscous oil, and that from the 1-1-4-4 diene, a reddish-yellow powder, formed in very small amount. The molecular weights were but slightly changed from those of the monomers, being 559 and 590 for the 1-2-3-4 and 1-1-4-4 products respectively.

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A QUANTITATIVE METHOD FOR MEASURING THE DETERGENT ACTION OF LAUNDRY SUPPLIES¹

BY O. M. MORGAN²

Abstract

An improved type of standard soil for measuring and comparing the detergent efficiencies of soaps has been developed. The technique of application of this soil to white, desized cotton sheeting has been studied with respect to obtaining a uniform product which is sensitive to small differences in washing procedure, both chemical and mechanical. The effects of time, temperature, soap concentration, and various rates of agitation have been investigated in connection with this soil. The results prove its sensitivity.

A miniature wash wheel has been constructed for use in the above work. It exhibits several improvements over small machines of this type formerly used.

Soap is recognized as the primary cleansing agent and the fundamental laundry supply. Statistics for the Dominion of Canada for the year 1929 show that approximately three millions of dollars was spent in the purchase of this product for commercial laundry purposes alone. This figure represents an increase over the previous year of 13.2%. A rapidly growing industry such as laundering requires scientific guidance in the proper channels. One of its most important problems is the choice of proper and efficient supplies. When these are obtained the next step is their efficient use to produce quality washing.

The science of laundering is one which contains many variables. Climatic conditions and geographic situation cause the type of soil on the fabrics to vary. Varying degrees of hardness of the water used offered difficulties to the industry until the introduction of lime-soda and zeolite water softeners. The art of stain removal has been studied very carefully and is now on a fairly satisfactory basis. However, no method has been evolved which has attained general acceptance for the quantitative comparison of one soap with another with respect to their washing powers. In order to determine and compare the washing powers of several soaps, a washing operation must now be actually carried out. The literature contains several papers recording experiments in which various physical properties of soap solutions were measured and the results interpreted to indicate detergent efficiency. The physical properties which have been measured in this connection are surface tension against air or oils, lathering power, emulsifying power, power of soap additions in the stabilizing of other emulsions or suspensions, and more recently the effect of the pH values. It has been definitely shown that these circuitous methods of arriving at detergent power, while being a certain amount of assistance, are not entirely satisfactory.

Previous Work

The literature on this subject up to 1928 is well reviewed in a paper by Rhodes and Brainard (6). The Detergents Committee of the American Oil Chemists Society has been working for several years in an effort to develop a

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test which will evaluate and compare detergent materials used in laundry practice. Their progress to date is reported by Vail (8). At present umber is being used as a soiling agent and is applied either in a Launderometer, or by dipping the samples, passing them through a wringer, and then rinsing in successive portions of clear water until the liquid remains clear. Washing is effected in a Launderometer and color changes after successive washes are checked with an Ives Tintometer or a Taylor Photometer as modified by Rhodes. No standard apparatus has been adopted as yet by the committee. Polesie (5) advocates the use of the step photometer for measuring brightness after consecutive washes. His article is very brief and no data are given.

Tate (7), in a recent article, brings forth a highly inadequate theory of detergency which may be completely disregarded. His postulates are thoroughly in error. Levitt (3) discusses the theories of detergency brought forward to date, namely, the Brownian movement theory, the lubricant theory, and the colloidal theory. Draves and Clarkson (1) discuss a new method for the evaluation of wetting agents which bears indirectly on the present subject. Lennox and Gilmore (2) present a large amount of data from plant tests concerning sudsing and rinsing time. Samples of wash liquor were centrifuged and the amount of insoluble dirt determined in this manner. This is the first work of this type on record and is on quite sound lines as far as insoluble dirt is concerned. Their conclusions are valuable to the industry in that they have determined the optimum times for the removal of solid dirt. Stain removal is not considered.

The main incentive to the present work was a paper by Rhodes and Brainard (6) in which it is claimed that a satisfactory method for the evaluation of the detergent efficiency of soaps has been worked out. It was, however, felt by the writer that some of the results might be rather misleading if considered as applicable to laundry practice. The method used by Rhodes and Brainard (6) was that of washing small samples of standardly soiled fabric in a miniature wash wheel (13.3 by 12.7 cm.) which was always driven in the one direction, usually at 80 r.p.m. The washing conditions were varied with respect to temperature, time, soap concentration, and rate of agitation. Inspection of the graphical results shown in their paper indicates immediately that the standardly soiled cloth was not sufficiently sensitive to small variations in the washing processes. The first illustration of this is in the comparison of runs at 20°, 40° and 60°C. The curves intersect at several places. A second illustration is presented in the runs at different rates of agitation. Here the 60 r.p.m. and 80 r.p.m. curves intersect and the final difference in brightness is of the order of 2% when compared with a baryta white standard.

The lack of sensitivity of the soiled fabric to washing is particularly apparent when the effect of the concentration of soap is investigated. Soap concentrations of 0.00, 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00% were used. With concentrations of 0.05% and higher no appreciable difference in washing power was noted.

When the increase in brightness produced by a given number of washes was

plotted against the time of one wash by Rhodes and Brainard (6), very sharp maxima in brightness were obtained at the end of a 7.5-min. washing period. If longer periods were used the dirt was redeposited in the fabric up to the 30-min. region, after which the curve flattened out and became practically parallel to the time axis. The washing conditions for obtaining these results were as follows:—Temperature, 40°C.; soap concentration, 0.25%; rate of agitation, 80 r.p.m. No satisfactory explanation of these maxima are given and similar work by the writer of this paper affords no evidence that they exist. This feature will be discussed more fully in a later section.

As a conclusion to their work, Rhodes and Brainard (6) ran tests on five intrinsically different soaps, namely, commercial soap flakes, potash-coconut oil liquid soap, powdered olive castile soap, tallow soap, and potassium oleate. The tests did not indicate any marked differences in detergent power. This would hardly be expected, due to the lack of sensitivity of the soil. "Indices of Detergent Power" were calculated. The validity of the values obtained is questionable due to several assumptions which are made in the calculations and also to the very slight differences in the detergent power obtained experimentally. In the opinion of the writer the Rhodes and Brainard (6) method of evaluating the detergent power of washing liquors is a step in the right direction but the method has not been subjected to sufficient refinements. The present paper deals with refinements of this method and is preliminary to a paper dealing with the detergent efficiency of neutral and built soaps.

Experimental

Soiling

After considerable experimentation with different soils it was concluded that a modification of the soil advocated by the Detergents Committee of the American Oil Chemists' Society was the most satisfactory. The formula is as follows:—Carbon tetrachloride, 2000 cc.; Russian tallow, 3 gm.; Nujol, 10 gm.; lampblack, 2 gm.

In a standard soil it is essential that ingredients which are as nearly standard as possible be used throughout. The A.O.C. soil contained tallow and lubricating oil. Wide variations in chemical properties may occur in these products; hence in the present work Russian tallow and Nujol were substituted. The former contains less unsaturated material and will not become rancid as ordinary tallow will. Nujol, a medicinal oil, has constant chemical properties and is much easier to obtain than a uniform grade of lubricating oil. A large quantity of lampblack was obtained from one source and stored in order that this product, which exhibits large variations in particle size, might be as uniform as possible. The carbon tetrachloride used was redistilled.

In preparing the soil batch the Nujol and tallow were dissolved in the carbon tetrachloride, the lampblack was added and the whole was agitated at a fixed constant rate for 15 min.

Prior to soiling, the cotton sheeting (Wabasso No. 55, thread count 82 by 68) was desized by first washing it twice with the white work in a local power

laundry, followed by a 90-min. treatment in 2% Diastafor. The fabric was then rinsed 10 times in distilled water, ironed dry, conditioned in a thermostatically controlled oven at 80°C. for one hour, and then air conditioned in the laboratory overnight.

One of the main objections to the Rhodes and Brainard (6) soil was that it was not sufficiently sensitive to small changes in washing procedure. This may be attributed to a large extent to the mode of application. The fabric samples were passed by hand through a portion of the soil mix until the proper shade of grey was obtained, blotted between several thicknesses of cheesecloth, dried in an oven at 80°C. for one hour, and then air conditioned for 11 hr. In the opinion of the writer this does not sufficiently impregnate the fabric with the soil mix, particularly the insoluble material, the lampblack. Only a surface coating is obtained.

The machine used in soiling the fabric in the present work is illustrated diagrammatically in Fig. 1. In reality this is a good quality household wringer set into a suitable framework. The rubber covered rollers (indicated by the numbers 2 and 3) of the wringer are operated by a chain drive from a motor and reducing gear not shown in the diagram. This insures a constant rate of drive. The whole mechanism is mounted on the platform *P*. The upper structure is hinged to the platform at *H* so that it may be tipped over in the direction of the arrow *A₄* to facilitate the removal of the soil trough *T*. The machine accommodates a strip of cloth 14 ft. long and 9 in. wide. The cloth travels in the direction of the arrows *A₁* and *A₂* and in doing so passes under roller 1 in the soil bath, between rollers 2 and 3 where excess soil is wrung out and flows back into the trough *T*, under roller 4, over rollers 5 and 6, and then back to the soil bath.

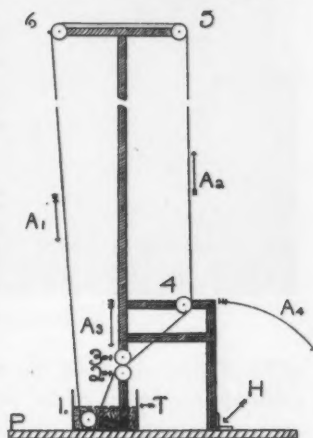


FIG. 1. Soiling machine.

Each complete circuit of the cloth requires one minute and each sample is given ten passes through the soil bath. An equalizing pressure of 25 lb. is maintained on rollers 2 and 3 as indicated by the arrow *A₃*. This is accomplished by a free moving lever hinged to the upright at one end of the rollers approximately six inches above them, and passing horizontally to beyond the outer edge of the upright on the opposite side. From this projecting end a weight is suspended. A metal pin of 0.25 in. diameter connects the lever arm to a spring which rides on the axle ends of the upper roller 3. This takes care of any minute irregularities which may be present in the rollers. The above procedure produces a very evenly soiled sample with a reflection of 11.5% as compared with baryta white. Soiled strips can be duplicated with satisfactory regularity. This will be corroborated with experimental data in a later section.

Washing

The miniature wash wheel used in this work, illustrated in Figs. 2 and 3, is an improved model of that used by Rhodes and Brainard (6). The improvements introduced with this machine are the following:—

(1) All metal parts coming in contact with the wash liquors are of Monel metal. (2) The machine reverses after a given number of revolutions, simulating the motion of a power laundry wash wheel. (3) The r.p.m. of the wash wheel may be widely varied as well as the number of revolutions before reversal.

The machine consists of a glass cylinder of 11.5 cm. diameter and 16.5 cm. long. Inside the cylinder is a Monel metal framework carrying six bars of 1 cm. diameter which correspond to the ribs in a laundry wash wheel. The ends of



FIG. 2. *Miniature wash wheel.*

the cylinder are closed by two Monel metal end plates containing counter-sunk rubber gaskets into which the glass cylinder fits. The end plates are connected outside the cylinder by six strong coil springs, thus forming a water-tight system. Through the centre of each end plate a Monel tube (1.2 cm. outside diameter) is fitted. These tubes are used for filling and draining the cylinder and at the same time act as trunnion bearings when the whole is mounted in the wooden housing illustrated in Fig. 2. A 150-watt light bulb supplies light and heat to the wheel and the temperature may be controlled to $\pm 1^\circ\text{C}$. The bulb is situated directly below the wash wheel and is protected from odd drops of water by a shield of fine copper gauze.



FIG. 3. *Wash wheel assembly dismantled.*

The driving mechanism, when the machine is driven constantly in one direction, consists of a motor and a reducing countershaft. When the machine is reversed after from one to three revolutions, the arrangement shown in Fig. 2 is used. A round leather belt is attached to a coil spring near the floor,

looped around the driving pulley on the wash wheel, and passes from there to the crank arm of the reducing gear. The wash wheel rotates in one direction until the crank becomes horizontal and then reverses for the same number of revolutions in the opposite direction. The number of revolutions before reversal may be altered by changing the length of the crank. The r.p.m. may be altered by supplying the motor and reducing gear with various sized pulleys.

To facilitate filling and draining the machine, the wooden housing is hinged at its base and may be tipped over on to the horizontal rests shown at the right. The lower end plate of the wash wheel is bevelled to the centre to insure complete draining. To insert and remove the fabric samples the upper end plate is removed.

The wash samples consist of a piece of standardly soiled cloth 10 by 20 cm. doubled, sewed up in bag form, and weighted with 100 gm. of glass beads of 3 mm. average diameter. Two of these bags are washed in 500 cc. of wash liquor in each operation.

Measurement of Whiteness

The criterion of the amount of washing which has taken place over a certain period is determined by measuring the brightness of the washed samples with a step photometer. A Zeiss Pulfrich photometer was used. This instrument is well described by Weltzien (9, pp. 46-53) and also briefly in the present connection by Morgan (4, p. 38).

Experimental Results

Testing Soil Batches

After soil batches were prepared as described in a previous section their washing properties were compared. A 0.25% neutral soap solution was used. This was prepared from a soap with the following analysis:—moisture, 2.01; total soap, 97.05; NaCl, 0.004; free alkali (Na_2O), 0.045; glycerol (by diff.), 0.89%; titer, 39.70°C. Washing and rinsing were carried out in the miniature wash wheel at 50°C., there being a 10-min. suds and two one-minute rinses in each operation. Each soil batch test consisted of two operations. The wash wheel was driven at 85 r.p.m. and reversed every 2.75 revolutions. All wash and rinse liquors were preheated to the desired temperature before introducing

TABLE I
RESULTS OBTAINED IN TESTING OF SOIL BATCHES

Wash No.	Batch number				
	1	2	3	4	5
	Percent brightness increase				
0	11.0	11.0	11.3	11.2	11.5
1	25.1	24.8	24.2	24.4	24.7
2	32.0	30.7	31.1	32.1	31.6

them into the wash wheel. Distilled water was used exclusively in all this work. Tests of this nature on five typical batches of soiled sheeting are included in Table I. It will be noted that the variations from one batch to another were comparatively small. Since each soiled strip was 14 ft. long, a large number of wash samples could be cut from each one. Comparisons of these samples gave identical results within the limit of experimental error.

Time Period Effect

The optimum length of time which a wash wheel should be operated in order to obtain maximum washing efficiency is a very important question. This has been investigated using washing periods of 2, 5, 7, 10, 20, 30, and 60 min. and temperatures of 25°, 50°, and 75°C. The data are presented numerically in Table II and graphically in Figs. 4, 5, and 6.

TABLE II
TIME PERIOD EFFECT DATA

No. of washes	Time period of one wash, min.						
	2	5	7	10	20	30	60
	Per cent brightness increase						
25° C.							
1	11.4	15.7	16.1	17.8	21.3	25.4	31.1
2	17.9	22.4	25.1	29.3	31.7	34.5	41.3
3	23.3	28.5	30.7	33.4	35.2	37.3	43.8
4	28.0	32.5	33.5	37.0	38.7	39.7	44.1
5	30.1	34.4	36.1	40.8	41.1	42.3	45.6
50° C.							
1	16.6	22.4	24.1	25.5	29.6	32.6	35.3
2	27.2	33.0	33.5	35.4	36.5	37.2	42.0
3	31.1	37.8	38.8	38.8	39.8	41.8	43.8
4	35.8	41.2	40.3	41.0	43.0	44.2	46.3
5	38.4	42.2	41.5	41.5	43.5	45.2	47.4
75° C.							
1	17.5	21.0	21.5	24.6	26.8	29.5	32.2
2	28.1	30.4	31.6	33.0	35.0	36.9	41.6
3	33.3	34.4	35.1	35.7	38.2	39.9	42.3
4	37.2	37.2	36.9	39.0	42.3	44.1	46.2
5	40.1	40.6	40.5	40.6	42.9	45.2	47.5

Each of the figures in the above tables was obtained by washing two samples of the standardly soiled fabric and taking the average of their respective increases in brightness. Each pair of samples was given five consecutive washes.

When total washing time is plotted against increase in brightness for each of the three temperatures, smooth curves are the result. This indicates uni-

formity in the soiling operation as well as in the washing operation. Only in one case do two curves intersect. This is in the 25°C. data where the 30-min. and 60-min. curves intersect in the 90-150-min. region. However, this region is relatively unimportant. The slopes of these curves would indicate that the optimum washing period lies in the 7-10-min. region. In practice, lightly

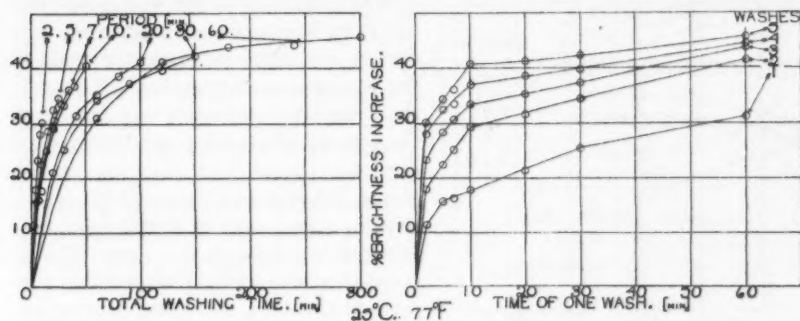


FIG. 4. Time period effect, 25°C.

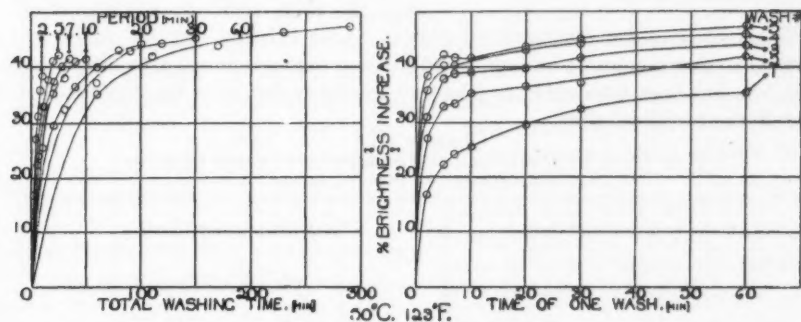


FIG. 5. Time period effect, 50°C.

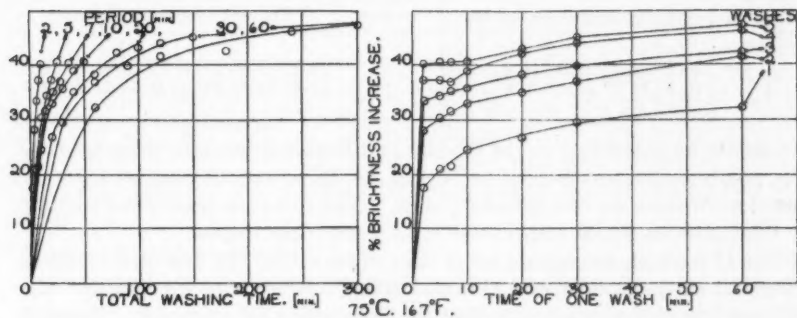


FIG. 6. Time period effect, 75°C.

soiled loads might be given a 7-min. treatment, and more heavily soiled loads a 10-min. treatment. If longer periods than 10 min. are used the efficiency decreases; shorter periods than 7 min. are very apt to be inefficient due to unstable emulsions or suspensions of the dirt being formed which would hinder it being rinsed free from the fabric.

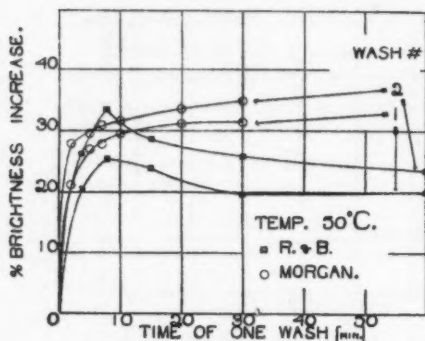


FIG. 7. Rhodes and Brainard (6) and Morgan's data compared.

with the Rhodes and Brainard (6) data in Table III and Fig. 7. After the second wash no maxima had appeared. Hence the experiment was discontinued. It has been impossible to give any logical explanation for the Rhodes and Brainard (6) maxima.

TABLE III
COMPARISON OF DATA OBTAINED BY RHODES AND BRAINARD WITH DATA OBTAINED IN THE PRESENT WORK

Rhodes and Brainard data						Data from present work						
No. of washes	Time period of one wash, min.					No. of washes	Time period of one wash, min.					
	3.75	7.5	15	30	60		2	5	7	10	20	30
	Per cent brightness increase						Per cent brightness increase					
1	20.7	25.2	23.2	19.8	19.9	1	21.2	27.0	27.8	29.5	31.2	31.3
2	26.8	33.0	28.5	25.8	23.6	2	27.8	29.5	31.0	31.7	33.6	35.1

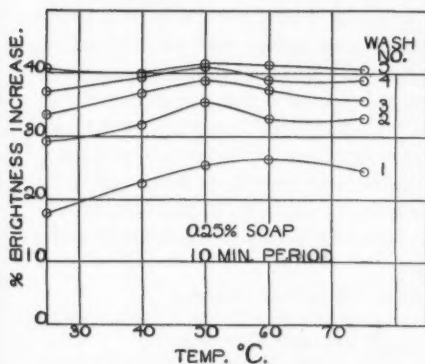
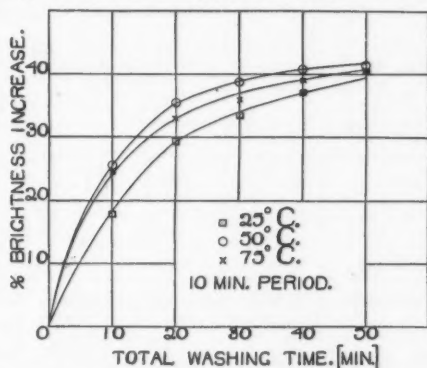
It should be noted that in the Rhodes and Brainard (6) data there are only three points in the curves prior to 30 min. to define the maxima while in the present work there are five defining points. This helps materially to eliminate any discrepancies which might arise in this important region.

Table II contains the second set of data obtained for the time period effect. In the first set no maxima were obtained with a 7.5-min. washing period. The work was repeated to make sure that the phenomena did not exist. Hence it is felt that this point has been conclusively proved.

Effect of Temperature

In Fig. 8 total washing time is plotted against per cent brightness increase for 25°, 50°, and 75°C. data considering 10-min. washing periods only. It will be noted that the 75°C. curve falls between the 25°C. and 50°C. curves indicating that the greatest washing efficiency is obtained at 50°C. In order to establish this optimum temperature more rigorously, washes were conducted at 40°C. and 60°C. The complete set of data for all temperatures investigated is presented in Table IV and illustrated graphically in Fig. 9 where temperature is plotted against per cent brightness increase for the five consecutive washes.

In all washes except the first the maximum detergent efficiency appears at 50°C. This is of more theoretical than practical interest since, in laundry practice, the first suds operation is always performed at a low temperature in order that albuminous material may be removed. If higher temperatures were used, the albumen would be coagulated and its removal from the fabric would be rendered very difficult.

FIG. 8. *Effect of temperature; 25°, 50°, 75°C.*FIG. 9. *Effect of temperature; 25°, 40°, 50°, 60°, 75°C.*

that the standard soil is sufficiently sensitive to indicate differences which do exist.

Effect of Soap Concentration

A further indication of the sensitivity of the standard soil used in the present work is furnished when the effect of soap concentration on detergency is investigated. Eight concentrations of soap were used ranging from 0.00 to

In laundry practice it is recognized that temperature has a definite bearing on soil removal. The type of standard soil used by Rhodes and Brainard (6) was not sufficiently sensitive to define clearly the temperature coefficient of detergency. The soil used in this work does show up temperature effects but it is illogical to advocate definite plant temperatures for optimum detergent effects until full scale operations have been thoroughly investigated. These investigations will be carried out at a future date. The point which the writer wishes to stress at present is

TABLE IV
EFFECT OF TEMPERATURE ON DETERGENT ACTION

No. of washes	Temperature, °C.				
	25	40	50	60	75
	Per cent brightness increase				
1	17.8	22.6	25.5	26.5	24.6
2	29.3	31.8	35.4	32.8	33.0
3	33.4	36.8	38.8	37.3	35.7
4	37.0	39.2	41.0	39.0	39.0
5	40.8	39.8	41.5	41.3	40.6

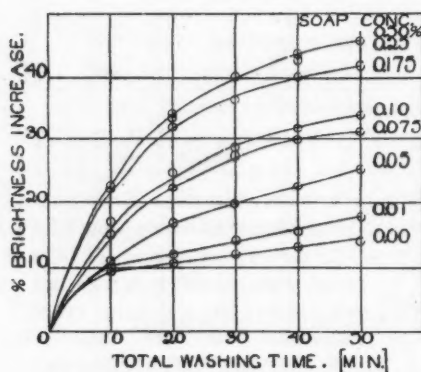


FIG. 10. Effect of soap concentration.

and Brainard (6) showed only very slight increases in detergent efficiency above a concentration of 0.01%. For higher concentrations their curves lie in one region and intersect in several places due, doubtless, to the lack of sensitivity of their soil. In standard laundry practice a soap concentration in the

0.50% by weight of dry soap. The washing conditions were as follows:—temperature, 50°C.; r.p.m. 85; revolutions before reversal, 2.75; formula consisted of one 10-min. suds and two one-minute rinses. The results are contained in Table V and Fig. 10.

There is a gradual increase in detergent efficiency until a maximum is reached at 0.25%. The curves for 0.25% and 0.50% concentrations intersect in two places and fall almost on top of each other so that only one curve but two sets of points are shown in Fig. 10.

In a similar experiment Rhodes

TABLE V
EFFECT OF SOAP CONCENTRATION ON DETERGENT ACTION

No. of washes	Soap concentration, % by weight of dry soap							
	0.0	0.01	0.05	0.075	0.10	0.175	0.25	0.50
	Per cent brightness increase							
1	9.5	10.3	11.1	17.0	15.7	22.5	23.0	22.4
2	10.7	12.1	16.8	22.5	25.1	32.0	33.5	34.2
3	12.2	14.4	19.9	27.6	28.6	36.6	40.3	40.2
4	13.3	15.7	22.9	29.8	31.7	40.3	43.5	42.5
5	14.2	17.7	25.6	31.3	34.0	41.8	45.4	45.5

region of 0.10% or slightly greater is maintained. From Fig. 10, considering only the present type of soil which is very difficult to remove, it is seen that this is quite an efficient concentration.

Effect of Reversing the Wash Wheel

Laundry wash wheels are driven two or three revolutions in one direction and then reversed. This prevents the load from rolling up into a ball-like mass and hindering the washing process. Also, at the time of reversal, there is vigorous agitation of the fabrics in the wash liquor. Experiments with the small wash wheel showed that, on the average, washing is 12.5% more efficient when the machine is reversed every 2.75 revolutions than when it is driven in one direction at the same rate. In these experiments the temperature was maintained at 50°C. and the rate of revolution at 85 r.p.m. The data are contained in Table VI and Fig. 11. Seven-, ten-, and twenty-minute washing periods were investigated.

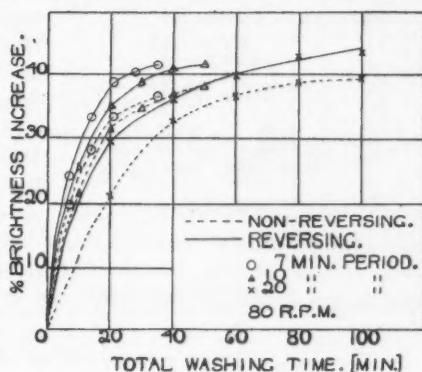


FIG. 11. Washing with a reversing and non-reversing machine.

TABLE VI
EFFECT OF REVERSING WASH WHEEL ON DETERGENT ACTION

No. of washes	Time period of one wash, min.					
	7		10		20	
	a	b	a	b	a	b
	Per cent brightness increase					
1	24.1	19.8	25.5	21.4	29.6	21.2
2	33.5	28.3	35.4	31.4	36.5	32.9
3	38.8	33.5	38.8	35.5	39.8	36.8
4	40.3	35.5	41.0	37.0	43.0	38.9
5	41.5	36.7	41.5	38.1	43.5	39.3

NOTE:—a, reversing; b, non-reversing.

Effect of Varying the R.P.M.

The experiments on the effect of varying the r.p.m. of the wash wheel were not conducted for the primary purpose of supplying data which could be applied directly to plant size machines, but to investigate the sensitivity of the standard soil to variations in the mechanical agitation during the washing process. This

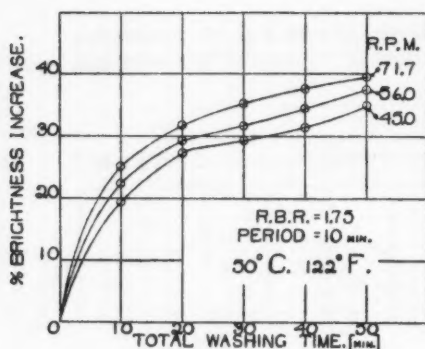


FIG. 12. Varying r.p.m.

factor is equally as important as the reaction of the soil to the supplies used in washing. Subsequent plant tests of a similar nature will provide data for the laundryowner.

It was found that the detergent efficiency increased with increasing rates of revolution. The temperature adopted was 50°C.; the period, 10 min.; the number of revolutions before reversal, 1.75; and the revolutions per minute, 45.0, 56.0, and 71.7. Table VII and Fig. 12 present the data obtained in these experiments.

TABLE VII
EFFECT OF VARYING R.P.M. ON DETERGENT ACTION

No. of washes	Revolutions per minute		
	71.7	56.0	45.0
	Per cent brightness increase		
1	25.2	22.4	19.3
2	31.9	29.4	27.4
3	35.3	31.6	29.3
4	37.6	34.5	31.2
5	39.6	37.5	35.1

Varying the Number of Revolutions Before Reversal

To investigate still further the effect of mechanical agitation on the standard soil the r.p.m. was maintained constant and the number of revolutions before reversal (R.B.R.) was changed from 1 to 1.75 to 2.75. The temperature was 50°C., the period 10 min. and the r.p.m. 70. Table VIII and Fig. 13 contain the results.

With an R.P.M. of 70 and R.B.R. values of 1, 1.75 and 2.75, the number of reversals is 70, 40, and 25 respectively. One would expect that the greater the number of reversals, the greater would be

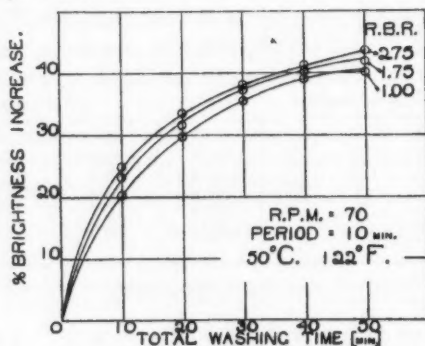


FIG. 13. Varying the number of revolutions before reversal.

the agitation, and that most efficient

washing would be obtained. However, this does not appear to be the case, since the best washing was obtained with 25 reversals, *i.e.*, 2.75 revolutions before reversal. This would indicate that there must be some sort of a balance between tumbling agitation and swirling agitation such as is obtained on the reversal. It would be a waste of time to go into this point more fully except on a plant scale.

TABLE VIII
EFFECT OF VARYING NUMBER OF REVOLUTIONS
BEFORE REVERSAL ON DETERGENT ACTION

No. of washes	Revolutions before reversal		
	1	1.75	2.75
	Per cent brightness increase		
1	20.1	23.2	24.8
2	29.7	31.6	33.6
3	35.5	37.4	38.1
4	39.0	40.3	41.3
5	40.1	41.8	43.6

It may be pointed out that the data in Table VIII are not comparable with other data listed in this paper. The soil batch from which these samples were cut did not check up with soil batches used in other parts of this work. Since only intercomparisons were required, it was considered sufficiently accurate for this part of the work.

Conclusion

The data contained in this paper show quite conclusively that the Rhodes and Brainard (6) method of determining the detergent efficiency of soap has been improved upon considerably. The improvements may be summarized as follows:—

- (1) The miniature wash wheel is constructed of non-corroding Monel metal. The ribs in the machine are of Monel metal and are not rubber covered.
- (2) The driving mechanism is capable of wide variations with respect to speed and reversibility.
- (3) The soiling procedure has been rendered uniform and consistent results are readily obtainable.
- (4) The soil is sensitive to small differences in chemical treatment and mechanical agitation during washing.

With the sensitivity of the soil, established work is now under way in which neutral and built soaps are being compared with respect to their washing power. The physical properties of their solutions are also under investigation. The results will be published in this journal upon completion.

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OIL DAMAGE TO COTTON TENTING MATERIALS¹BY O. M. MORGAN²

Abstract

The effect of weathering on white and brown (Mineral Khaki) cotton duck tenting materials treated with a variety of oils has been investigated. Vegetable oils have the greatest deteriorating action. Cottonseed oil has been shown to produce the greatest weakening effect, giving tensile strength losses of 73% during a 240-day exposure. Mineral oil exerts only a moderate damaging effect. It is possible that the tensile strength losses are proportional to the iodine values but this has not been definitely established. Mineral Khaki has a very definite weather-proofing and oil resisting action when impregnated in cotton.

Several months ago two damaged tent tops were submitted, by the Department of National Defence, to this laboratory for inspection. The damage appeared to have been caused by oils, as the fabric was quite rotten where oil spots occurred. A search of the literature revealed very little helpful information. Phair and Lukash (1) in a recent paper discuss oil damage to cottons in laundering after exposure to sunlight. Losses of as much as 49% in tensile strength were experienced with cottonseed oil after sun treatment for 48 hr. and then washing. In the dark after 14 days the loss was 10%.

The amount of oil added to each sample was not stated. The treatment, however, consisted of impregnating the samples with oil, exposing them in the light and also in the dark, and then making tensile strength tests before and after washing. The authors conclude that the damage may be attributed to two causes. The first is the fact that the oils lubricate the fabric. The second is their power to absorb oxygen, or oxidize. Drying oils, possessing this property to a marked extent, oxidize and weaken the cotton fibres. Tests for oxycellulose are readily obtainable after the above treatment. Light accelerates the oxidation.

No data on heavy fabrics such as duck were available.

Experimental

New samples of white and brown duck were obtained, treated with a variety of oils, stretched on a frame, and exposed to the weather on the roof of the laboratory from April 15 to December 11, 1931. The frame was tilted considerably to give the samples a southern exposure. After 125 days' exposure each sample was divided and one-half was brought into the laboratory for tensile strength tests.

The characteristics of the new samples of duck are contained in Table I.

It may be seen that the white and the brown samples are identical as far as weave is concerned. The brown duck had been treated with "Mineral Khaki" (2, p. 897). It was found to have an ash content of 1.75% containing iron-chromium salts and a trace of silica. This is a fast dye and a good weather-proofing agent.

The chemical characteristics of the oils used are given in Table II.

¹ Manuscript received January 29, 1932.

Contribution from the National Research Laboratories, Ottawa, Canada.

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TABLE I
PROPERTIES OF DUCK SAMPLES USED

Type of duck	Tensile strength, lb.	Thread count		Ply of yarn		Chemical treatment
		Warp	Filling	Warp	Filling	
White	150.4	50	30	3	4	— Mineral Khaki
Brown	165.4	50	30	3	4	

TABLE II
PROPERTIES OF OILS USED

Oil	Type	Acid value	Iodine value
Mineral lubricating	Non-drying	0.33	12.7
Linseed	Drying	2.46	177
Cottonseed	Semi-drying	0.44	109
Castor	Non-drying	1.00	85

Each sample of duck, 5 by 24 in., was sprayed with 20 gm. of oil dissolved in 25 cc. of ether to facilitate spreading.

Tensile strength tests were made using a Suter tensile strength machine with 1-in. jaws, a throw of 12 in. per min., and accommodating a sample 3 in. long. Table III shows the tensile strength losses after oil treatment and weathering.

TABLE III
EFFECT OF EXPOSURE AFTER TREATMENT WITH OILS

Type of duck	Exposure, days	Per cent tensile strength losses with:—				
		No oil	Mineral oil	Linseed oil	Cottonseed oil	Castor oil
White	125	4.2	14.8	59.5	68.8	50.6
	240	9.1	22.4	66.7	73.0	57.1
Brown	125	0.7	10.7	26.3	29.2	12.8
	240	1.2	19.6	27.3	34.1	13.9

In order to determine the loss in tensile strength due to the lubrication of the fabric by the oil a similar set of oiled samples were prepared. These were allowed to stand for 24 hr. after spraying in order that the oil might soak into the fabric. Losses in strength were very similar for all the oils used. The white duck showed an average loss of 8.9% and the brown duck 6.3%.

Discussion

Inspection of Table III indicates that the amount of damage by the oils falls in the following order: cottonseed, linseed, castor, and mineral lubricating

oil. This order holds true for both the white and the brown duck. Hence, it may be concluded that vegetable oils are more damaging to cotton materials than mineral oils.

In the case of white duck, with the exception of linseed oil, the tensile strength losses are proportional to the iodine values of the oils. Linseed, since it is a drying oil and hardens on the fabric, may supply a certain amount of protection against weathering after the hardening is complete. The losses in strength suffered by the brown duck are not proportional to the iodine values of the oils.

The apparent relationship between the tensile strength loss of the white duck and the iodine values of the oils with which it was treated may be merely fortuitous. The relationship may, however, be a causal one. Further work would be required to decide the point definitely.

Duck treated with mineral khaki presents the following valuable characteristics—

(1) In weathering tests where no oil is present over a 240-day period its loss in tensile strength is 1.21% as compared with 9.11% for white duck.

(2) In weathering tests where vegetable oils are present its total tensile strength loss is 40.8% lower on the average than that of white duck. When mineral oil is used it is 2.8% lower.

(3) Oil does not penetrate nor lubricate mineral khaki duck to the same extent that it does white duck. The lubrication loss in tensile strength for the former is 6.3% and for the latter 8.9%. It is impossible to differentiate between losses due to weathering and lubrication after the samples have been exposed for some time, since the lubricating properties of the oils change to a marked extent. This is particularly true in the case of drying and semi-drying oils.

It is strongly recommended that tents, tenting materials, sail cloth, or cotton fabrics of any kind should not be stored or transported in close proximity to oil drums, oily machinery, or the like. Especial care should be taken to avoid their contact with vegetable oils. Also, oil spots should be removed immediately upon detection by using organic solvents such as ether, chloroform or carbon tetrachloride.

Acknowledgments

The writer wishes to thank the Department of National Defence, Ottawa, for supplying the new samples of tenting materials used in this work, and Mr. C. W. Davis of this laboratory for analyzing the sample of brown duck.

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THE COMPARISON OF GASEOUS DENSITIES BY THE METHOD OF BALANCING COLUMNS¹

BY ARTHUR H. SNELL² AND A. NORMAN SHAW³

Abstract

An application of the principle of balancing columns to the comparison of gaseous densities at any ordinary pressure is described. The precision of a given apparatus depends upon the heights of the columns, on the sensitivity of the pressure gauge, and on the extent of uncontrolled fluctuations in temperature. Without a thermostatic control and employing a simple modified form of the Toepler micromanometer with columns 12 m. in height, a sensitivity of 10^{-7} gm. per cc. is obtained. The apparatus and the technique are explained in detail, with a discussion on the elimination of errors. An application of the method is made in the field of hygrometry, and its usefulness in the measurement of air-gas ratios is also explained and recommended. An advance in precision is obtained, primarily by the use of an improved form of Toepler micromanometer.

Introduction

If two gases of different densities are placed respectively in two closed vertical columns, the pressure being kept the same at the tops, then the difference in density of the gases will produce a difference in the hydrostatic pressure at the bases of the columns; or, conversely, it can be stated that the reading of a suitable pressure gauge connected between the bases of two such columns is a measure of the difference in density between the gases which they contain. This is the principle involved in the "balancing columns" method of comparing the densities of gases or gaseous mixtures.

Romberg and Blau (1) applied the method to wet and dry air, in developing an absolute hygrometer based on the determination by this method of the difference in density between the sample to be tested and a standard sample of saturated air. The same principle had also been tried roughly by one of the present writers, using an inclined gauge which gave results of too low an accuracy to be of practical interest. The present investigation was originally intended to be a development of this method, with the greater precision which might be expected from higher columns, the use of a standard column of dry air instead of saturated air, and improved methods of measuring the small pressure difference which is developed at the bottom. It was soon found, however, that the usefulness of the method is by no means confined to hygrometry, and that its possibilities as a means of comparing gaseous densities in general have not been fully realized; the former is only one field of many in

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NOTE BY A. N. SHAW: A preliminary account was presented verbally at the meeting of the Royal Society of Canada in Toronto, in May, 1931. This work was part of an investigation on hygrometrical problems carried out under a grant from the National Research Council, by Mr. A. H. Snell, acting as my assistant. Some promising initial tests had been made by Dr. H. W. Harkness, Acadia University, while acting in the same capacity and the scheme had been considered theoretically, but apart from general supervision and advice the whole of this investigation on the method of balancing columns as reported in this paper has been developed by Mr. A. H. Snell.

which the method may be useful. At the same time, however, it should be pointed out that to use the balancing columns as a hygrometer is to subject it to a performance test of a most rigorous nature.

In the course of the investigation considerable experience was gained and some advances were made in the use of the Toepler tilting micromanometer. The simplicity and low cost of the instrument, coupled with its great sensitivity, recommend it for many purposes now served by more elaborate and expensive micromanometers. It was accordingly considered useful to include in this paper some remarks on the performance of the instrument, together with an account of some improvements in its design.

Theory of the Method of Balancing Columns

In a vertical column of gas the contribution to the pressure at its base which is made by a small layer of gas at a distance x from the top, and having a thickness dx , is given by

$$dp = g\rho dx. \quad (1)$$

The relation between p and ρ may be obtained from the equation $p\nu = RT$, or, if greater accuracy is desired, from one of the more elaborate equations of state. Let us, for a close approximation, take the relation given by Van der Waals' equation in the form

$$p\nu = RT + Bp,$$

where $B = b - \frac{a}{RT}$, a and b being the familiar Van der Waals' constants. This gives

$$\rho = \frac{\frac{pM}{RT}}{1 + \frac{Bp}{RT}}, \quad (2)$$

where M represents the molecular weight of the gas. Substitution of this value for ρ in Equation (1) followed by integration gives

$$RT \log p_B + Bp_B = gMh + RT \log p_A + Bp_A,$$

where p_A and p_B refer respectively to the pressures at the top and the base of a column of height h . This in turn can be written in the form

$$\frac{p_B - p_A}{p_A} - \frac{1}{2} \left(\frac{p_B - p_A}{p_A} \right)^2 + \frac{B}{RT} (p_B - p_A) = \frac{gMh}{RT},$$

where terms in the third and higher powers of $(p_B - p_A)/p_A$ have been neglected.

Further rearrangement and the elimination of M by virtue of Equation (2) leads readily to the form

$$p_B - p_A = \frac{gh\rho_A}{1 - \left\{ \frac{1}{2} \frac{p_B - p_A}{p_A} \left(1 + \frac{Bp_A}{RT} \right) \right\}}$$

where ρ_A represents the density of the gas at the pressure p_A . Now the terms Bp_A/RT and $(p_B - p_A)/p_A$ are both so small that their products and higher powers may be found on substitution in the present problem to be negligible. It is therefore evident that the expression reduces to

$$p_B - p_A = gh\rho_A \left(1 + \frac{1}{2} \frac{p_B - p_A}{p_A} \right) = gh\rho_A \left(1 + \frac{1}{2} \frac{gh\rho_A}{p_A} \right).$$

Since B does not survive in this expression it is now apparent that the simple equation of state, $pV = RT$, is adequate for our present purpose.

Similarly for a column of the same height but containing a different gas,

$$p'_B - p'_A = gh\rho'_A \left(1 + \frac{1}{2} \frac{gh\rho'_A}{p'_A} \right).$$

Now if the columns are connected across the top, $p_A = p'_A$, and consequently the difference in the pressures at their bases (*i.e.*, the pressure registered by the pressure gauge) is given by

$$\Delta p = p_B - p'_B = gh(\rho_A - \rho'_A) \left(1 + \frac{1}{2} gh \frac{\rho_A + \rho'_A}{p_A} \right) \quad (3)$$

(It is convenient to use the symbol Δp to represent the small difference in pressure at the bases of the columns).

This final expression may be regarded as the general operating formula for the balancing columns. In the great majority of cases the last term on the right-hand side will be found to be negligible. Only with heavy gases in long columns will it have an appreciable effect*. Thus for general use the formula usually reduces to

$$\Delta p = gh(\rho_A - \rho'_A),$$

or simply

$$\Delta p = gh(\rho - \rho'), \quad (4)$$

where ρ and ρ' represent the respective densities of the two gases at the pressure and temperature prevailing at the time of the experiment.

Discussion of Temperature Effects

To avoid difficult measurements and calculations it is obvious that the two columns should be kept as nearly as possible at the same temperature. In order to do this it was found most convenient to place one column inside the other. In practice three possible types of temperature variations yet remain in this arrangement, which may affect the reading of the pressure gauge at the bottom of the columns. They are as follows: (i) simultaneous equal changes in temperature affecting both columns; (ii) a variation in temperature from point to point up each column, such variation being equal in the two columns because of their close contact; (iii) a small fluctuating difference in temperature between the two columns.

Of these we might expect each of (i) and (ii) to balance out on the two sides of the gauge, and therefore have no effect upon its reading. This is obviously true of (i), but it is necessary to examine (ii) and (iii) in some detail.

In case (ii) let us suppose that there is the same linear temperature gradient up each column. This gives a rough idea of what to expect in practice since the temperature gradients which are apt to be encountered will be nearly equivalent to linear along portions of the columns. Let the temperature at the top of the columns be T_A , and at their bases, T_B . Then, if G signifies the temperature gradient, we have $G = (T_B - T_A)/h$.

**E.g.*, with columns 12 m. in height, filled with bromine and xenon respectively, the inclusion of this term would produce a change of about 0.6% in the value of Δp .

It is apparent from Equation (1) that at a distance x from the top

$$dp = \frac{\rho M}{R(T_A + Gx)} g dx.$$

On integrating from top to bottom and applying to the case of two columns as before, we get

$$\Delta p = \frac{\rho_A g h \log (T_B/T_A)}{R (T_B - T_A)} (M - M') = gh (\rho - \rho') \left(1 - \frac{T_B - T_A}{T_A} \right).$$

Thus the effect of an equal and uniform temperature gradient up both tubes is merely to multiply the Δp deduced on the assumption of a zero temperature gradient by the factor

$$\left(1 - \frac{T_B - T_A}{T_A} \right). \quad (5)$$

It can be seen from this that a difference in temperature of 6°C. between the top and the bottom of the columns would be required to alter the value of Δp by 1 part in 100. A difference in temperature as large as this would rarely be encountered in practice.

In case (iii) there must be free intercommunication between the columns at the top, or otherwise an exceedingly slight variation in temperature (say one ten-thousandth of a degree) will be sufficient to disturb the pressure gauge sufficiently to make the reading hopelessly inaccurate*.

Let us suppose that one column is placed inside the other, and that both are initially at the temperature T . The temperature of the outer column is then raised to T' , thus introducing a temperature difference of $T' - T$. Let V_0 = volume of outer column; V_i = volume of inner column; A = area of cross section of the annular outer column; a = area of cross section of inner column; ρ_0 = initial density of gas in outer column; ρ'_0 = final density of gas in outer column; ρ_i = initial density of gas in inner column; ρ'_i = density of original gas in inner column if imagined to occupy $V_i - v$; v = volume of gas of density ρ_0 passing from the outer to the inner column through the connecting tube at the top.

Then after the temperature change has taken place the outer column will be filled with gas of density ρ'_0 ; while the inner column will contain a mixture which will be equivalent to a height $(h - v/a)$ of gas of density ρ'_i , and a height v/a of gas of density ρ_0 . Thus the change in the pressure difference between the bases of the columns will be given by

$$\delta (\Delta p) = gh (\rho_i - \rho_0) - \left\{ g \left(h - \frac{v}{a} \right) \rho'_i + g \rho_0 \frac{v}{a} - g \rho'_0 h \right\}.$$

Noting that $(V_i - v)\rho'_i = V_i \rho_i$, that $(V_0 + v)\rho'_0 = V_0 \rho_0$, and also that $v = V_0 V_i (T' - T) / T (V_0 + V_i)$ approximately, it can be shown that the above expression reduces to

$$\delta (\Delta p) = gh \rho_0 \frac{T' - T}{T}. \quad (6)$$

It will be noted that this is also very nearly the change in the gauge reading

* It was, in fact, observed that when the columns were joined at the top by a capillary tube 1 mm. bore and 4 cm. long, the fluctuations observed by the pressure gauge made accurate reading impossible.

which would be produced if the gas in the outer column had been allowed to expand into the air instead of into the inner column. It is important to notice that the effect of the volume v of gas of one density being mixed with gas of the other density is itself negligible in the case under consideration. The transfer of the volume v exerts its influence only in that it permits a relative change in density in the columns when a temperature difference is maintained.

To obtain an idea of the magnitude of these effects suppose that the outer column of an apparatus

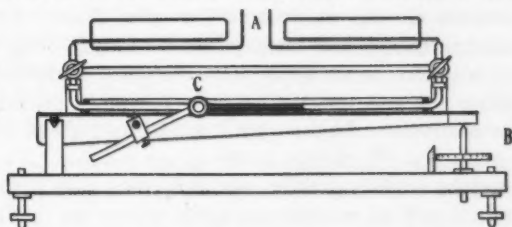


FIG. 1. The Toepler micromanometer as modified for use with the balancing columns. The fine tubes lead from A to the bases of the columns. B is the tilting screw, and C is the microscope used for observing the meniscus of the manometer liquid (shown black).

having the dimensions of that described below is raised 0.01°C. above the inner column. Then, if both columns were originally at 20°C. , it is found that $v = 0.03 \text{ cc.}$ Also if the outer column were filled with dry air $\delta(\Delta p) = 0.05 \text{ dynes per cm}^2$, which is so small as to approach the limit of accuracy of the reading of the Toepler gauge. It is thus apparent that to be used to its full advantage an apparatus of these dimensions should be designed to keep the average differential temperature fluctuations between the columns within the bounds of 0.01°C. If this is impossible the experimenter must be content with diminished accuracy, but it would require fluctuations of about 0.3°C. to produce an error of 0.1% in ρ_i/ρ_o .

The obvious way to eliminate all disturbing temperature effects is to enclose the columns in a thermostat. This would, however, involve an elaborate and usually unnecessary addition to the technique. In measurements in which an accurate knowledge of the temperature of the columns is not required (e.g., in the balancing columns hygrometer and in the measurement of air-gas ratios) one of the main advantages of the method lies precisely in the fact that high precision can be obtained without sacrificing simplicity in the apparatus. It is apparent that in any given case the constancy of repetition of the micromanometer readings will indicate whether or not the temperature control is adequate.

Discussion of Diffusion Effects

During any given determination the connecting tube at the top of the columns is open, and a small amount of diffusion must necessarily take place in both directions which, after a long time, will alter the difference in pressure at the bottom. A simple calculation shows that during the average time taken to make an observation with the micromanometer gauge the resulting correction will be negligible. It can be shown that this correction is given approximately by multiplying the right-hand side of Equation (4) by the factor

$$\left\{ 1 - \frac{D \Delta t}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \right\}, \quad (7)$$

where D is the coefficient of the diffusion for the two gases at the temperature of the experiment; a is the area of cross section of the connecting tube, and l is its length; V_1 , V_2 are the volumes of the two columns; and t is the time in seconds during which diffusion takes place. In columns of the dimensions used in the present tests, joined by a connecting tube 10 cm. long and 4 mm. in bore, this factor would have the value 0.99973 in the case of diffusion taking place for one minute between columns containing carbon dioxide and air respectively. At this rate it would take about 40 min. for diffusion effects to produce a 1% change in the gauge reading. For other gases the value of D may be slightly greater, but it appears that with the given columns diffusion effects will be entirely negligible unless the readings cover an extremely protracted length of time.

The Use of the Balancing Columns as a Hygrometer

The difference in density which exists between dry air and damp air suggests the use of the columns as an absolute hygrometer. The sample of air which is to be tested can be placed in one column and balanced against a standard column of either dry air or saturated air. The use of a column of dry air is preferable because saturated air may lead to difficulties, as described below.

Dry and Damp Columns

For the present purpose it is adequate to assume for the density of the damp air the usual expression $\rho = 1.293 \times 10^{-3} \times 273 (P - 0.378f)/760T$, where P denotes the barometric pressure in mm. of mercury, f the partial pressure exerted by the water vapor (also in mm. of mercury), and T the absolute temperature. Since the density of dry air is given by $1.293 \times 10^{-3} \times 273P/760T$, we have from Equation (4),

$$\Delta\rho = gk \times 1.293 \times 10^{-3} \times 273 \times 0.378f/760T,$$

whence

$$f = 760T\Delta\rho/(gk \times 1.293 \times 10^{-3} \times 273 \times 0.378),$$

and

$$H = 100 \times 760T\Delta\rho/(gk \times 1.293 \times 10^{-3} \times 273 \times 0.378F),$$

where H denotes the percentage relative humidity of the damp air, and F the maximum vapor pressure of water in millimetres of mercury at the temperature T . This may be written in the form

$$H = C T \Delta\rho / F \quad (8)$$

where C is a constant for the columns used. This may be regarded as the operating formula for the balancing columns hygrometer using a standard column of dry air.

Variations in the carbon dioxide or oxygen content of the air may be sufficient to cause changes in density which, if attributed solely to water vapor, might in extreme cases cause errors of several per cent of relative humidity in the measurements given by the columns. This possibility is eliminated in practice by drawing a new sample of dry air into the standard column whenever a new sample of damp air of the same kind is introduced into the other column.

Saturated and Damp Columns

If the air sample of unknown humidity is balanced against a standard column

of saturated air instead of dry air, reasoning similar to that given above leads to the expression

$$\Delta p = gh \times 1.293 \times 10^{-3} \times 273 \times 0.378(F-f)/760T \quad (9)$$

This, however, assumes a pressure gradient in the vapor part of the column. If the walls of the column are wet we might expect that no such gradient would exist. On calculating the value of Δp from this point of view we get

$$\Delta p = gh \times 1.293 \times 10^{-3} \times 273(F - 0.378f)/760T \quad (10)$$

—a value considerably larger than the foregoing.

There is a small variation in the saturated vapor pressure F of a liquid with the external pressure p given by $dF/dp = V_1/V_2$ where V_1 is the volume of unit mass of the liquid, and V_2 that of unit mass of its vapor. Calculation shows that this is negligible in the present case.

A number of readings were taken using a column of saturated air which had been prepared by pouring a small quantity of water down one of the tubes. The values of Δp obtained were intermediate between those expected according to Equations (9) and (10), but were grouped chiefly about the former. Temperature effects in the saturated column made the readings exceedingly variable. It is clear that in the vicinity of the state of saturation temperature variations will have an exceptionally large effect, not covered by the reasoning already developed for unsaturated or dry gas samples.

Application to the Measurement of Gaseous Ratios

The balancing columns may be used to determine the proportions by volume of the constituents in a mixture of two gases.

Let ρ'_1, ρ'_2 be the densities of the two constituent gases in the mixture, and let ρ_1, ρ_2 be their densities if each is reduced to the pressure of the mixture,

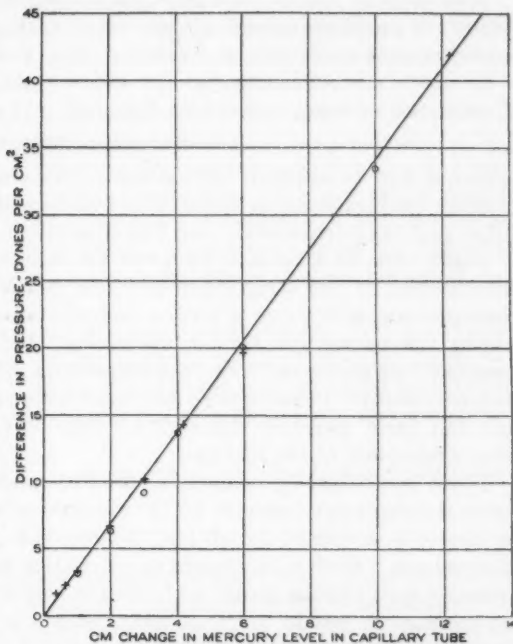


FIG. 2. Results of calibration of two Toepler micro-manometers. The straight line gives the theoretical relationship between the changes of level of the mercury in the capillary tube and the pressure changes thereby produced. The points ○ give the experimental values given by one gauge, using xylol as a manometer liquid; and the points + those given by the second gauge, using normal butyl phthalate.

the temperature being unaltered. Under these conditions let their volumes be v_1 and v_2 respectively. Let ρ be the density of the mixture, and let r be the percentage by volume of the first constituent in the mixture, *i.e.*, $r = 100 v_1/V$ where V is the volume of the mixture. Then it is apparent that

$$\rho = \rho'_1 + \rho'_2 = (v_1 \rho_1 + v_2 \rho_2)/V = \{r \rho_1 + (100 - r) \rho_2\}/100,$$

and therefore

$$r = 100(\rho - \rho_2)/(\rho_1 - \rho_2). \quad (11)$$

Now suppose that we have one column containing the second gas in its pure state. If we fill the second column in turn with the mixture and with the first constituent, we will obtain values for $(\Delta p)_1$ and $(\Delta p)_2$ where,

$$(\Delta p)_1 = gh(\rho - \rho_2) \quad \text{and} \quad (\Delta p)_2 = gh(\rho_1 - \rho_2).$$

Comparison of these results with Equation (11) shows that

$$r = 100(\Delta p)_1/(\Delta p)_2 = 100 n_1/n_2, \quad (12)$$

where n_1 and n_2 represent the number of divisions of the tilting screw of the Toepler micromanometer required to compensate for the pressure differences $(\Delta p)_1$ and $(\Delta p)_2$ respectively (see Equation (13)).

Aside from its simplicity the great advantage of this method is that it is independent of the composition of either constituent of the mixture. This consideration is of value in testing such mixtures as air and coal-gas; *e.g.*, in rating commercial gas heating appliances. In such tests it is required to measure "air-gas ratios"—*i.e.*, the proportions in which air and gas are mixed before burning. Other devices have been improved recently for this purpose (2), but their operation and accuracy may be limited by the variability of the composition of the coal gas.

When the balancing columns method is applied to measurements of this type, it is most convenient to fill the standard column with air, and to balance against it a sample of the air-gas mixture and then a standard sample of the coal gas. With a micromanometer reading to 0.1 dyne per sq. cm. the columns need only be about one metre in height in order to measure r with an accuracy of within 0.1% of gas. Such precision is itself an improvement upon other instruments now in use, but if a simple compact instrument is not essential the use of the more delicate micromanometer with longer columns should easily improve the accuracy tenfold or more, temperature effects being the ultimate limiting factors.

Experimental

The Micromanometer

The tilting micromanometer devised by Toepler is particularly adapted for use with the balancing columns on account of its sensitivity and simplicity of construction. It consists essentially of a manometer tube in the shape of a very flat V mounted on a tilting table. One of the menisci is observed through a microscope fitted with a cross-hair. It is best used as a null instrument.

If the micrometer tilting screw must be turned through n divisions to compensate for the shift due to a pressure difference Δp at the ends of the tube,

and if φ is the angle of tilt corresponding to one of these divisions, then the value of Δp is given by

$$\Delta p = g\rho n\varphi\lambda, \quad (13)$$

where ρ is the density of the liquid and λ the horizontal distance between menisci (3). This expression disregards meniscus corrections. They are in general negligible in work with the balancing columns, for the pressure differences to be measured are usually small, and with a convenient value of λ (e.g., 10 to 20 cm.) the angles of tilt involved in measurements are not large enough to introduce them to an appreciable extent.

For work with the balancing columns the original Toepler gauge was modified to the form shown in Fig. 1. The manometer tube is shunted through two three-way stopcocks by a second tube. This arrangement is convenient for setting the gauge to its zero position; it also increases the rigidity of the instrument. The fine, looped tubes which connect the ends of the manometer tube to the bases of the columns are made by drawing out a piece of 1-cm. glass tubing to arm's length, and bending it to the required shape in a yellow flame. Wax joints connect them to the columns and to the gauge. Their purpose is to eliminate distortion or strains in the manometer tube when the latter is tilted. Without these precautions and modifications, appreciable errors in the readings were produced on tilting.

Following Toepler, xylol was used as a manometer liquid. It has a slight disadvantage in that its vapor attacks stopcock grease. Ordinary kerosene also proved to be satisfactory. Normal butyl phthalate was tried because of its low vapor pressure, but it was found too viscous to make quick reading possible.

A sensitivity of better than 0.03 dynes per sq. cm. was obtained with this micromanometer.

Calibration of Micromanometer

A preliminary arrangement of the balancing columns apparatus gave results which were very irregular (due probably to distortion in the then unimproved gauge), and at the time it was thought that the trouble might arise from some unforeseen errors in the readings given by the micromanometer. To test this point it was decided to give the instrument an independent calibration. This was done by connecting it between two gas reservoirs one litre in capacity, and compressing the gas in one reservoir by from 1 to 40 parts in a million by adjusting the level of a thread of mercury in a capillary tube connected to that volume. To decrease the inevitable temperature effects as much as possible two Dewar flasks were used as reservoirs, and they were placed side by side in a water bath. The effect of temperature changes in the connecting tubes was reduced to a minimum by using tubes 0.5 mm. in bore, and by lagging all exposed parts with asbestos string. The importance of these precautions becomes evident when it is borne in mind that, with a closed volume on each side of the gauge, the temperature fluctuations had to be reduced to the magnitude of about 10^{-4} °C.

It was necessary also to avoid any bending of the connecting tubes when the

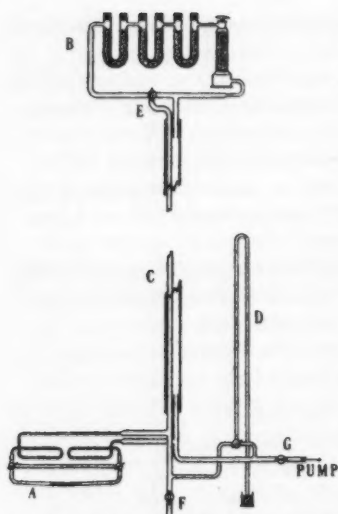


FIG. 3. The balancing columns apparatus arranged for use as an absolute hygrometer. The two columns are shown at C, one inside the other. The outer column contains the dry air, and the inner column the air whose humidity is to be measured. The Toepler micromanometer A is connected across their bases. By suitable manipulation of the three-way cock E the tops of the columns may be connected (a) directly (for taking readings); or, (b) through the drying system B (for introducing new air samples, as explained in the text).

liquids were subjected to the calibration, and the results of the test are given in Fig. 2. The straight line gives the theoretical pressure differences produced by given changes in the capillary tube assuming the compression or expansion to be purely isothermal.* The various points are the readings obtained from the gauges in the manner outlined above. The fact that the points lie upon the line within the limits of experimental error shows that the gauges were accurate within the pressure range used. This is good evidence of the reliability of this type of micromanometer.

The procedure followed in this calibration can be extended to the measurement in general of small pressure differences in confined spaces. It was found, for example, that the pressure gradients in discharge tubes could be investigated by connecting exploring tubes respectively to each side of the gauge. The gauge may also be of use in testing instruments which depend either upon the

gauge was being tilted, since the minute volume changes which are incurred were found to vitiate the accuracy desired. The whole apparatus was therefore mounted on the tilting table, so that it moved as a unit during adjustments of the micrometer screw.

The residual temperature effects caused persistent drifts of the gauge meniscus in one direction or the other. Since these drifts were for the most part regular, it was found possible to correct for them by taking alternate timed readings of the tilting screw when the mercury was at the upper and at the lower of two chosen positions of the capillary tube scale. By plotting these screw readings against time two roughly parallel curves were obtained. The mean of a number of readings of the distance between the curves was then taken as the number of screw divisions required to counterbalance the difference in pressure produced by a change in the mercury level from one of its two chosen positions to the other.

This procedure was followed for pressure changes ranging from 1.5 to 40 dynes per cm^2 . Two different gauges with different

*It might appear that the conditions of this test imply an adiabatic change, but the pressure changes were slow and were so minute that the thermal capacity of the containers rendered the operation nearly isothermal, as was found by comparison with larger and faster compressions. The insulation of the vacuum flasks was necessary, for the influence of external temperature fluctuations could not be reduced sufficiently in any ordinary thermostat.

maintenance of constant pressure or the accurate measurement of small changes, e.g., gas-thermometers and absorption hygrometers.

The Procedure with the Columns

In testing the performance of the balancing columns it was decided to return to the use of the apparatus as a hygrometer. Because of the very small difference in density between damp and dry air the precision obtained in humidity measurements is a much more rigorous test than can conveniently be devised by such methods as balancing known samples of mixed gases.

The apparatus is shown diagrammatically in Fig. 3. The two columns are shown at *C*, one inside the other. They had an effective height of 1213 cm., the outer consisting of an iron pipe and the inner of copper tubing, respectively 2.3 and 0.8 cm. in internal diameter; the external diameter of the inner tube was 1.0 cm. They were in contact in many places throughout their lengths, which assisted in reducing differential temperature fluctuations. The micro-manometer is shown at *A*. *B* is a drying system; it consists of three large U-tubes containing pumice impregnated with sulphuric acid, and a drying tower containing phosphorus pentoxide. *D* is a mercury manometer, which may be connected at will to the outer column or to the inner column.

When humidity readings of the room air are to be taken, the inlet stop-cock *F* at the base of the inner column is opened, and the three-way cock at *E* is turned so as to deflect an upward-flowing air stream to the left. The pump is started and the cock *G* is opened to an extent sufficient to cause an air stream to flow at moderate speed into the apparatus at *F*, up the inner column, through the drying system from left to right, down the outer column, and out to the pump. The rate of streaming is judged by the reading of the manometer *D*, which is connected for this purpose to the outer column. When the old air in both columns has been replaced by new samples (*i.e.*, after several minutes of streaming) the pump is stopped, *F* and *G* are closed, and *E* is turned through 180 degrees, thereby short-circuiting the drying system and putting the two columns into unobstructed communication at the top. The micromanometer reading is then taken, and the relative humidity is calculated from Equation (8). It may be deduced at any desired temperature merely by inserting the appropriate values of *F* and *T**.

A series of measurements were taken in this way, and they were checked independently by a ventilated wet and dry bulb hygrometer of the Assmann type. The relative humidity given by the columns was calculated at the temperature of the dry bulb. The Assmann hygrometer was in turn checked by a chemical hygrometer.

Constancy of Readings on Repetition

The specimen readings in Table I are given to illustrate the accuracy obtained with the apparatus on repetition. Several readings of the difference

*A combination of Equations (8) and (13) indicates that at a given temperature the number of screw divisions required to balance the columns is directly proportional to the relative humidity of the air in the damp column; this shows that the apparatus can be made to read directly in percentage of relative humidity at a certain fixed temperature merely by a suitable choice of scale on the tilting screw.

TABLE I
SAMPLE READINGS TAKEN WITH THE BALANCING COLUMNS SHOWING THE
ACCURACY OF REPETITION OBTAINED

(1)	(2)	(3)	(4)
Δp dynes/cm. ²	Difference in density, gm./cm. ³	Δp dynes/cm. ²	Difference in density, gm./cm. ³
8.53	7.34×10^{-6}	8.85	7.44×10^{-6}
8.95	7.52	8.89	7.48
8.95	7.52	8.99	7.56
8.96	7.53	9.06	7.62
		8.91	7.50
		8.94	7.52
Mean, 8.90	Mean, 7.48×10^{-6}	Mean, 8.94	Mean, 7.52×10^{-6}

in pressure produced by two given samples of air are given in column (1), the corresponding density differences in column (2); the same two samples balanced on the following day gave the readings recorded in columns (3) and (4). The average deviation from the mean of all of the values of the difference in density given in the table is 0.055×10^{-6} gm. per cc. Such precision indicates that more elaborate temperature control is hardly necessary in ordinary measurements.

Fig. 4 gives a comparison between the values of the relative humidity obtained from the columns, and the corresponding values as measured by the Assmann instrument. A good linear agreement is shown for the humidity range covered. In this particular test the samples of damp air were all balanced against a common sample of dry air.

It will be observed that in the above test there is an average discrepancy

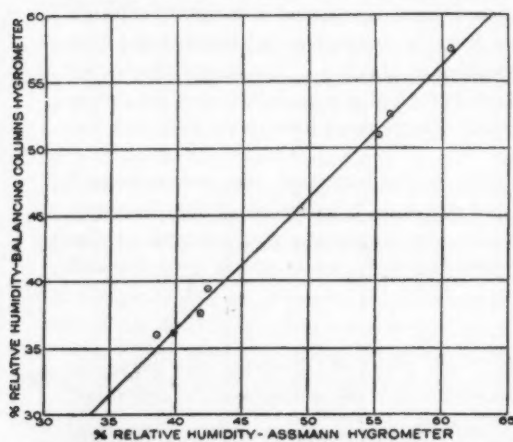


FIG. 4. Comparison of humidity measurements of room air taken with the balancing columns and with the Assmann hygrometer.

of about 3% between the Assmann readings and those from the columns. This is due to the density of the constant sample in the reference column, which was not quite dry; it will be seen that, to obtain close agreement, it is merely necessary to move the graph parallel to itself by an amount equal to the correction. Subsequent careful repetitions and thorough preparations of the reference sample reduced this difference, but as the range covered in each of the later tests was less, the above record was

chosen to illustrate the linear agreement. Isolated comparisons ranged from 0% to 100% in relative humidity and, with the exception of those near saturation (for reasons already given), the same general agreement was obtained.

The departures of the points in Fig. 4 from the straight line are due to four factors: (i) experimental error in readings from the columns; (ii) experimental error in the Assmann readings; (iii) variations in the carbon dioxide content of the damp air samples; (iv) errors due to the fact that the Assmann gives the mean relative humidity of a large quantity of air, taken over a comparatively long period of time, while the columns give the humidity of only a small sample.

Of these (i) is the only one strictly associated with the balancing columns method; the other three are involved, as before, only in the means chosen to test the apparatus. Results such as those given in Table I remain the best criterion for judging the precision obtainable, and indicate that (i) is very small. It appears that the balancing columns can measure density differences to about 0.1×10^{-6} gm. per cc. even with temperature control of the simplest nature, and that the method shows promise of still greater precision if the temperature fluctuations are reduced further.

A large number of tests were made with various samples of prepared moist air, and also with mixtures of carbon dioxide, all of which provided no further information beyond confirming the usefulness and sensitivity of the method. It had been hoped to check the sensitivity closely by the use of samples of gas graded in density and measured independently, but in all such attempts the accuracy of the present method appeared greatly to surpass that of the procedure by which it was being tested.

Acknowledgment

The writers wish to acknowledge the assistance of Dr. H. W. Harkness in the preliminary tests.

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A PIEZO-ELECTRIC METHOD OF MEASURING THE PRESSURE VARIATIONS IN INTERNAL COMBUSTION ENGINES¹

By H. G. I. WATSON² AND D. A. KEYS³

Abstract

A piezo-electric pressure gauge is described in which the pressures produced by the explosions in an internal combustion engine are recorded as the displacements of the beam of a cathode-ray oscillograph. By applying a time displacement, synchronizing with the speed of the engine, to the beam so as to cause a displacement at right angles to the pressure displacements, the time-pressure characteristics of the engine explosions are obtained on a photographic film. This arrangement reduces the inertia of the gauge to a minimum and is of special value in obtaining records of a single cycle in the investigation of knocks. Specimen records taken on a Petter hot-surface engine are given.

For the efficient study of the best working conditions in the modern internal combustion engine, it is necessary to determine the pressure variations in the cylinders of such engines when running under different conditions. There are many different types of indicators, but the ideal instrument should be as free from any inertia effects as possible in order that rapid variations in pressure, such as those given by knocks, may be accurately indicated. When this investigation was begun, all the methods which had been used for studying the pressure variations in internal combustion engines involved the inertia of a diaphragm. The method used by the writers involves a practically massless indicator.

The piezo-electric method of measuring pressures applies the property possessed by some crystals of becoming electrified when subjected to pressure (3, 14). The crystals of tourmaline and quartz possess this property, and when sections of these crystals are cut in the appropriate direction, it has been shown (2, 12, 13) that the charge produced on the surface of the sections is directly proportional to the total pressure applied. This piezo-electric property of tourmaline has already been used by one of the authors (6, 7) for determining the type of pressure waves formed when mixtures of water, gas and air are exploded at constant volume, and when charges of gun-cotton and T.N.T. are detonated under water. Karcher (5) has used the piezo-electric properties of quartz to determine the pressures in guns.

The preliminary results obtained by the method described below were presented at meetings of the Royal Society of Canada (8, 9). The method consists in having a number of quartz crystals suitably mounted in a holder which may be screwed into the engine cylinder. The pressure in the engine is communicated to the crystals without inertia, except that involved in a pressure wave passing through the crystals. The electric charge generated is directly proportional to the pressure on the crystals and is amplified by a special type

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of vacuum-tube amplifier, the resulting potential changes being recorded on a cathode-ray oscillograph. With this combination, the variations in pressure are transferred into similar variations in electric charge, which in turn are measured by the deflection of the cathode-ray beam of the oscillograph, the combination thus constituting a practically inertia-less pressure gauge. The cathode-ray oscillograph is so constructed that the vertical displacement of the beam is proportional to the pressure, and a horizontal motion of the beam is made proportional to the time. Such a combination was used by S. Watanabe (15) for internal combustion engines, but no attempt was made to give the pressure-time calibrated curves, the author indicating that his results showed the possibilities of the method. A more recent paper by J. Kluge and H. E. Linckh (10) gives the time-pressure curves for a rather low pressure engine, using the piezo-electric indicator and a string galvanometer for registering the variations in potential.

The apparatus used by the writers consists of the following parts: (i) the crystal detector which is screwed into the engine; (ii) the amplifier; (iii) the oscillograph; (iv) the uniform time scale apparatus; (v) the calibration apparatus.

The Crystal Detector

A diagram of the crystal detector is shown in Fig. 1, which is drawn to scale. It consists of a steel block *ABC*, *AB* being threaded to fit the spark plug opening of an ordinary gasoline engine. *M* is a standard spark plug with the central rod extended and bent to *N* as shown. The preliminary experiments were made on a Ford engine, but later a type of hot-surface Diesel engine was used, known as a Petter hot-surface oil injection engine. As this engine does not need a spark ignition, the lower part *ABVCM* of the detector was replaced by a nipple that was screwed into the side at the top of the engine. Over the other opening is placed the thin steel diaphragm *D*, about $\frac{1}{8}$ in. thick, through which the elastic pressure wave is transmitted to the crystal system. The plate *D* acts merely as a gasket. *JJ* is a steel tube for holding the piezo-electric crystals, and this tube is screwed into *AC*. A bakelite tube *SS* lines the steel tube *JJ*. Into the lower end of *SS* is fitted a steel rod of the shape shown at *E*, and on top of this six quartz crystals *F*, each one inch in diameter, are placed, a piece of lead foil between each crystal. The crystals are inserted in such a way that the positive face of the first is down, *i.e.*, in contact with *E*. The second crystal is placed with its positive face up, the third with positive face down, and so on as indicated in the diagram. When this battery of crystals is compressed, it will be seen that three of the inside plates become negatively charged, and the other two inside lead plates and the extreme ends of the system of crystals become positively charged. The three negatively charged plates are connected by a wire which runs in a groove in the bakelite, to an insulated binding post *K*. The positively charged surfaces are connected together and to the metal hemisphere *G*, which is placed on the top. A steel cap *II* is screwed on the end of the tube, and a steel screw *H* passes through this cap and presses on *G*. When the crystals are all inserted, *H* is screwed

up very tightly so that the crystals are all pressed firmly together and the whole is pressed down against the plate *D*. *K* will now be found to be charged negatively as a result of this pressure of the screw *H*, but this charge is removed by connecting *K* with the case *AB* or the engine into which the apparatus

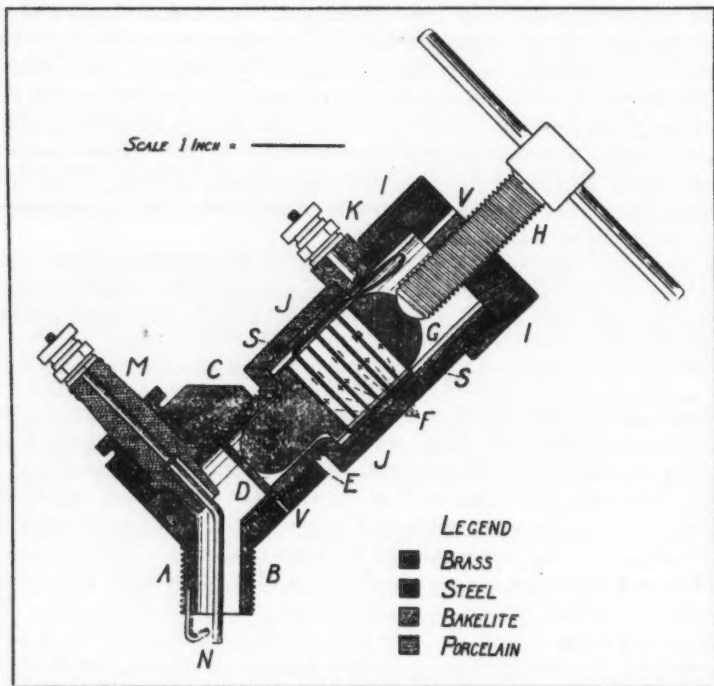


FIG. 1. The crystal unit.

is screwed. The pressure from the explosion in the cylinder of the engine acts on the plate *D*, which does not move appreciably, however, but only transmits the pressure as an elastic wave to the crystals *F*. This additional pressure causes *K* to become charged negatively with a charge of electricity which is proportional to the pressure. If the pressure on *D* becomes less than the normal amount, *i.e.*, if there be a rarefaction in the cylinder of the engine, then *K* will become positively charged with a charge which again is proportional to the rarefaction in the cylinder. Thus any pressure changes in the engine are transformed by this detector into similar variations in the potential of *K*, the only inertia effect in the system being the wave through the metal *D* and *E* and crystals. The natural period of vibration of the detector will be of the order of 10^{-5} sec. The binding post *K* is connected to a resistance-coupled amplifier, the engine being grounded. The oscillograph grounding is accomplished through the conductive networks of the amplifier circuit.

The potential to which the terminal K of the detector is raised by a given pressure will depend upon the number of crystals used. There is, however, an optimum number, n , to obtain the maximum voltage of the system for a given pressure. We have a limited length of the pressure unit for practical reasons. Suppose the length is l and the area of cross section of each crystal is A . Let q be the charge produced on each face of a crystal by the applied pressure. If K is the dielectric constant of the quartz, the capacity, c , of each crystal condenser neglecting edge effects, will be approximately $\frac{KA}{4\pi n l}$, since the

thickness of each crystal will be $\frac{l}{n}$. Hence $c = n \frac{KA}{4\pi l} = nx$. The capacity of the n crystals in parallel will be $nc = n^2x$ where x is a constant equal to $\frac{KA}{4\pi l}$. The total charge produced will be nq . Thus if the external capacity is C_x , we have for the voltage V , the relation $V = \frac{nq}{n^2x + C_x}$. By differentiation it follows that V is a maximum when $n^2x = C_x$, *i.e.*, when the capacity of the detector equals the external capacity. In these experiments only six plates were used, as that was the largest number that could be put into the space, the quartz available being about 3 mm. thick. About four times this number would have been better, had there been available facilities for cutting thinner quartz plates, the capacity of the detector being about 60 micromicrofarads. Such thin plates, however, would break easily, so it was considered that the thicker plates, though fewer in number, would be more practical. Also the leakage over the plates would increase with the number.

In order to keep the leakage effect as small as possible the crystal detector was shunted with a good mica condenser, the capacity of which would be varied from 0.001 to 0.006 microfarad. This reduced the potential of K , produced by the pressure, and consequently the error due to leakage of the charge was proportionally lower. These small variations in potential produced across the condenser by the charge from the crystals must then be amplified, and applied to the deflecting plates of the oscillograph.

The Amplifier

Much thoughtful work was devoted to the proper type of amplifier, for the success of the method depends on the adequate functioning of this part of the apparatus. The final form decided upon is shown in Fig. 2, and is a two-stage resistance-coupled aperiodic amplifier in which the first stage is replaced by a bridge-type arrangement. This method has the advantage that the disturbing effects of changes in battery potential, filament operating current and other small extraneous disturbing forces are minimized. It is also possible to keep the valves working on the particular part of the characteristic desired. The two-tube bridge circuit has been described by Nottingham (11), and the general arrangement of the two stage amplification by Arnold (1).

Without entering into the details of this type of amplifier here, it will be sufficient to state that the crystal detector is shown at C , and the condenser in parallel at C_x . Variations in the potential across C_x , due to pressure

changes on C , cause a change in potential of G_1 , the grid of the valve T_1 . This throws the "bridge" out of balance with the result that the potential of G_2 is altered causing a change in the potential across the resistance R_3 . By operating the tubes on the appropriate characteristic smooth parts of their curves,

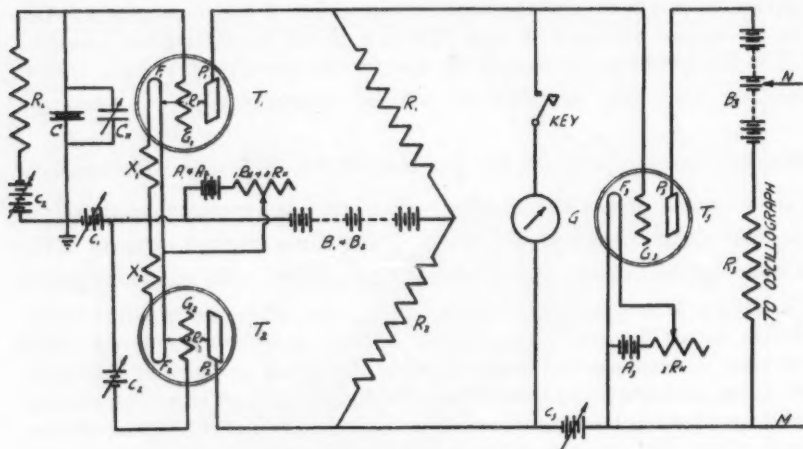


FIG. 2. The amplifier circuit.

it is possible to obtain a constant amplification factor for the range of changes of potential assumed by C_s due to the pressure variations in the engine. One pair of deflecting plates of the oscillograph are connected across the resistance R_3 , a number of the cells of the B-battery B_3 being included in order to keep the spot, caused by the cathode-ray beam of the oscillograph, on the screen. The key and high resistance galvanometer G are included in the circuit for testing the balance of the bridge circuit, the necessary alternations in R_1 , R_3 , X_1 , X_2 and C_s being made so that small changes in plate battery voltages, and in the main battery rheostat, do not change the current through the galvanometer (which need not necessarily be zero). The potentials of the batteries C_1 , C_2 , C_3 and C_s could be varied. R_1 and R_2 were made 150,000 ohms each. R_L was 100 megohms, X_1 and X_2 being small adjustable resistances for compensating any small variations in filament battery voltages. R_3 was 100,000 ohms. The battery voltage B_1B_2 was 180 volts, and B_3 also 180 volts of which about 100 were included in the oscillograph circuit. The characteristics of each valve were determined and they were operated on the linear portion of the plate current-grid voltage curve. Since the apparatus was calibrated *in situ*, the actual amplification of the system need not be known.

The Oscillograph

A low voltage cathode-ray oscillograph of the J. B. Johnson type, such as that supplied by the Western Electric Company, was used (4). This instrument is provided with two pairs of deflection plates very nearly at right angles. The

one pair of plates is connected to the amplification terminals NM , Fig. 2. This pair was so arranged that the deflections due to variations in potential across NM were in a vertical plane. The vertical deflection of the spot on the screen was thus proportional to the potential across NM , and this in turn was directly proportional to the potential across the capacity C_x , which varies, as already stated, as the pressure in the cylinder of the engine. Hence the vertical displacements of the cathode-ray beam are proportional to the pressures in the engine.

The second pair of plates in the oscillograph are connected to the timing device and these plates cause the spot to move in a horizontal direction with uniform velocity. The timing could be altered so that the time required for the beam to swing from one end of its path to the other agreed with a single cycle of the engine, and thus a time-pressure pattern, which would appear stationary to the eye, would be traced on the screen. By having the oscillograph in a dark room, it was found that the amount of light from a single transit of the beam on the willemite screen was sufficient to leave a record on a photographic film, when the film was placed with its sensitive side directly against the glass screen of the oscillograph. As a rule the pattern repeated so well that several transits could be photographed, giving a consistent uniform picture on the film. When artificial knocks were produced the single excessive pressure, due to the premature explosion, was plainly visible on the photographic record. For reproduction purposes, it is necessary to give multiple transit pictures, which are more diffuse than the single transit records.

The Uniform Timing Circuit

The timing circuit which was used is shown in the diagram, Fig. 3. The terminals F and G are connected to the time deflection plates of the oscillograph, G being the common terminal of the plate system of the Johnson oscillograph.

D is a voltage regulating tube of the "Radiotron" UX 874 type. B is a battery, the voltage of which may be varied from 90-135 volts, to regulate the mean voltage across the condenser C , which is also the potential across FG , in order that the cathode-ray beam will describe a path sym-

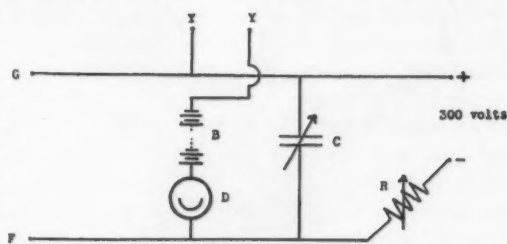


FIG. 3. The time scale circuit.

metrically, between the two deflecting plates of the oscillograph, of the proper length. The capacity of the condenser C could be varied from 0.001 to 1000 microfarads. The terminals YY were short circuited during an exposure, but a contact on the flywheel of the engine could be inserted between YY in order to give on the oscillograph the position of the piston with respect to the time scale. A 300-volt battery connected in series with a variable high resistance R (0.02 to 20 megohms) was connected across the condenser C . We thus have

the equation for the voltage V across the condenser C at any time t from the moment the battery is connected given by $V = E(1 - e^{-\frac{t}{RC}})$, where E is the total potential of the battery (300 volts), C the capacity of the condenser and R the resistance. By altering the values of R and C , the time constant of the circuit may be arranged so that the periodicity of the breakdown of the tube D will coincide with the period of the cycle of the engine. By the choice of this resistance and capacity with the voltage E being 300 volts, only the first part of the exponential growth curve is used and this may be made to differ from a linear relation by a negligible amount. In the apparatus used it was practically linear within the limits of the experimental error in measurement.

With this timing device stationary figures of the time-pressure curve were obtained on the oscillograph when the engine was running at a uniform speed. It was found incidentally that the regularity of the neon voltage regulating tube was very much improved when the tube was illuminated with the light from a 40-watt lamp. This was apparently due to a small photo-electric effect which made the tube break down with precision when a definite potential was reached. Such a lamp was placed beside the Radiotron tube, and the whole enclosed in black cloth to keep the room dark during the taking of a photographic record.

The Calibration of the Crystal Detector

The crystal detector was removed from the engine and screwed into a special form of hydrostatic calibration apparatus shown in Fig. 4, the whole system

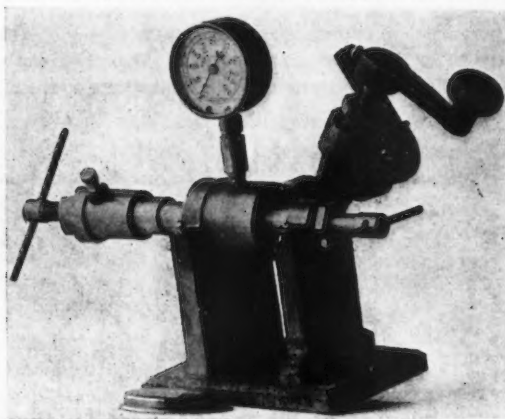


FIG. 4. Pressure calibration apparatus.

remaining otherwise in the same condition as used in obtaining the oscillographic record of the time-pressure variations in the engine. The pressures were applied to the detector by screwing up the plunger until the oil pressure reached a given value as indicated by the gauge. The charge was then removed from the oscillograph plates and the pressure suddenly released by opening the valve. Under these conditions the charge produced on the

detector will be equal, but of opposite sign, to that produced by applying the same pressure. Since the pressure can be released more rapidly than applied, this method was used in calibrating the apparatus, as the time for any leakage was reduced to a minimum. The deflection of the spot on the oscillograph was then measured for a given pressure. In this way there was obtained a pressure

calibration curve which was found to be practically linear. Two examples of such curves are given in Fig. 5. When the batteries become run down, the curve is no longer linear. The calibration curve taken when the above records were made is shown in Fig. 5, *B*, the calibration curve *A* representing the results when the battery potentials are well up. The capacity in the circuit in the two cases was different, the capacity used in the case of curve *B* was 0.004 microfarads. This method of calibration avoided the necessity of determining the amplification factors, capacity of the system and other constants, since these quantities all remained constant.

The gauge was later calibrated against known pressures applied on an apparatus loaned for the purpose by Dean Ernest Brown of the Engineering Faculty. It was found that the authors' gauge did not read correctly, but a good correction curve was obtained. It thus became possible to transfer the oscillograph pressure displacements into actual pressures measured in pounds per square inch, as shown in Fig. 5.

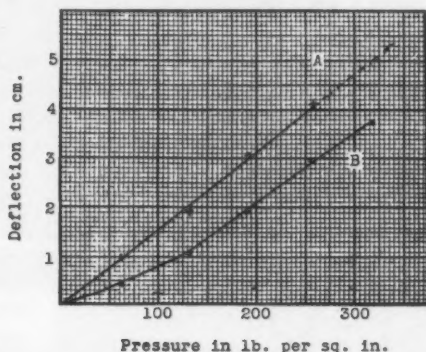


FIG. 5. Pressure displacement calibration curves.

Results

A number of photographs were taken of the time-pressure curves with the apparatus described above. The Petter hot-surface engine, of the Mechanical Engineering Laboratory at McGill University, was used, and records were obtained for different loads and also for various values of the capacity in parallel with the crystal detector. Records of knocks artificially obtained in the engine were also secured.

To illustrate the type of result which has been achieved, prints from two typical records are shown in Figs. 6 and 7 taken under similar working conditions of the engine, but with different values of the capacity in parallel with the detector. The net load on the brake balance in each case was 20 lb. It will be seen that both curves have the same general shape but the one shown in Fig. 7 has a higher maximum displacement than the other. This is due to the smaller capacity used in taking the record shown in Fig. 7. The pressure displacements in the two cases will be inversely proportional to the capacities used. The capacity used in the first case was 0.004 microfarad, and in the second 0.003 microfarad, their ratio being 1.33. Thus 1.4 is approximately the ratio of the maximum displacements.

These records are time-pressure curves but it is usual to indicate the volume-pressure relations. The time scale has thus to be converted into a volume scale. This may be done by using the contact on the flywheel of the engine

in the timing device shown at YY in Fig. 3. The position of this contact on the wheel relative to the position of the piston in the cylinder is known and thus a definite point on the time scale is related to the position of the piston. From a knowledge of this fact, it is possible to transfer the time scale to a volume scale. This has been done in the case of the curve shown in Fig. 6, supposing the crank to be very much smaller than the connecting rod, which is approximately so in this engine. For accurate computation a method such as that suggested by Kluge and Linckh (10) must be followed. The results

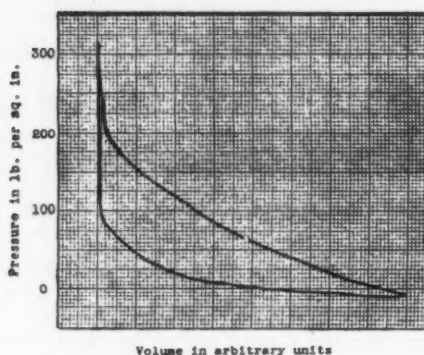


FIG. 8. Pressure-volume curve by piezo-electric gauge.

are shown in Fig. 8. In Figs. 6 and 7 the pressure displacements will have different scales, owing to the different capacities used in taking the records as already explained. By comparing the maximum displacements with the calibration curves the maximum pressure in the case of Fig. 6 was found to be 314 lb. per sq. in., whereas in the case of Fig. 7 it was 307 lb. per sq. in., a result in good agreement. These curves indicate that the method duplicates observations satisfactorily. For comparison, a print from a record taken on this engine seven years ago with the Cambridge Mechanical Indicator is

shown in Fig. 9. In shape at least the two methods give similar results.

To compare the authors' results with the maximum pressures obtained by using the Bureau of Standards type of balanced pressure diaphragm indicator, Professor R. H. Patten, of the Mechanical Engineering Department, very kindly took the readings shown in Table I, with the engine used by the writers.

TABLE I
RESULTS OBTAINED WITH THE WRITERS' ENGINE USING THE BUREAU OF STANDARDS
TYPE OF BALANCED PRESSURE DIAPHRAGM INDICATOR

Load, lb.		2	5	10	15	18	21
Readings, lb. per sq. in.	Min.	180	210	220	290	300	315
	Max.	260	250	260	300	310	320

The authors used a load of 20 lb. in obtaining the curves shown in Fig. 6 and 7; the mean result is about 311 lb., a value in good agreement with the above.

Records of knocks artificially produced by pre-ignition were obtained. The record is perfectly clear, but the single transit does not affect the film sufficiently strongly for reproduction purposes. As an example, for one record the maximum pressure was 321 lb. per sq. in., while the engine was running, the pressure rising at the knock to 562 lb. per sq. in. Such a knock is a very

PLATE I



FIG. 6. Time-pressure curve using a shunting capacity of 0.004 microfarad.



FIG. 7. Time-pressure curve using a shunting capacity of 0.003 microfarad.

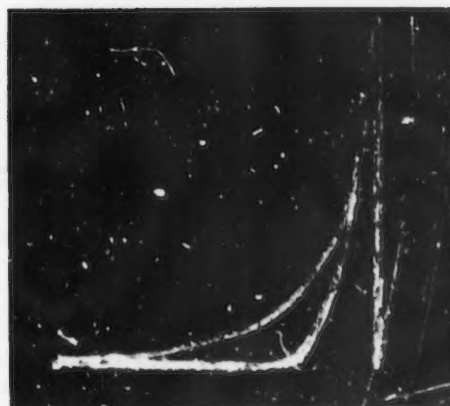


FIG. 9. Cambridge mechanical indicator diagram of same engine.



sudden affair, and it is under these conditions that the method using the cathode-ray oscillograph has an advantage over any mechanical indicator, or a device in which a galvanometer is used.

The results obtained in this investigation show that the piezo-electric pressure gauge in conjunction with the cathode-ray oscillograph may be successfully used as an inertia-less indicator for internal combustion engines. The new Von Ardenne cathode-ray oscillograph, owing to the greater intensity of its beam, would give single transit records that could readily be photographed.

Acknowledgment

The writers wish to express their thanks to the Department of Mechanical Engineering, McGill University, for permission to use the engine on which these tests were made.

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